

Thermal- and Electron Impact-induced Decarbonylation of Tropones: a Comparison of Neutral and Radical-cationic Pericyclic Reaction Mechanisms

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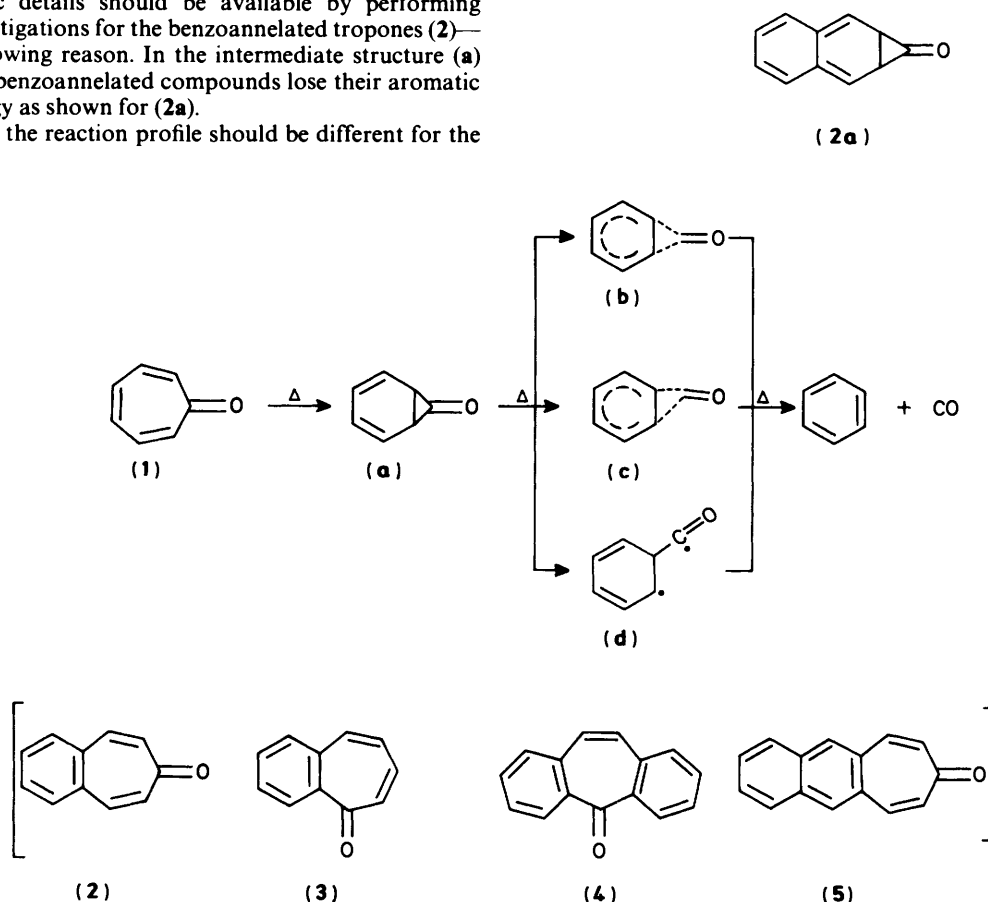
The neutral and radical-cationic decarbonylation of tropone and benzoannulated tropones is experimentally investigated by pyrolysis and electron-impact mass spectroscopy, respectively. The reaction mechanisms are discussed by means of MNDO calculations. From these results it is deduced that the thermal reaction proceeds in two steps, the first one being an electrocyclic ring closure while the second, rate-determining step, consists of the cheletropic CO extrusion. The cationic reaction also starts with the (rate-determining) ring closure. However, the norcaradienone ion opens to a benzoyl-type ion, which is the actual precursor of the CO loss. The effect of the benzoannulated substitution is different for the thermal and cationic reaction profile.

Comparable mechanisms are postulated for the apparent similarity of the thermal-¹ and electron impact-² induced CO loss of tropones, which, by ring fraction, preferentially yield aromatic systems. The reaction can be explained by a sequence of symmetry-allowed pericyclic reactions,^{1,3,4} as depicted for the thermal decarbonylation of tropone (1) in Scheme 1.

In our previous paper,^{3a} we compared the neutral and cationic CO loss of tropone experimentally and by means of semiempirical (MNDO) SCF calculations. A deeper insight into the mechanistic details should be available by performing analogous investigations for the benzoannulated tropones (2)–(5) for the following reason. In the intermediate structure (a) (Scheme 1) the benzoannulated compounds lose their aromatic resonance energy as shown for (2a).

The effect on the reaction profile should be different for the

neutral $4n\pi$ -electron systems compared with the $4n-1\pi$ -electron radical cations. Thus, the influence of the resonance energy on the reaction profiles can be studied. This prompted us to carry out a mass spectrometric investigation of the CO loss of the benzoannulated tropones (2)–(5) and to compare the results with the products formed in the pyrolysis reaction,⁵ as well as with previous data for unsubstituted tropone.^{3a} The mechanisms of both the thermal- and electron impact- (EI) induced processes



Scheme 1.

Table 1. CA spectra of $C_{10}H_8^{+}$ ions (m/z 128) derived as $M - CO^{+}$ ions from benzo[*a*]tropone (2) and benzo[*a*]tropone (3) compared with naphthalene M^{+} . The intensities are relative to the sum of collision induced fragment ions

| [<i>m/z</i>] | (2-CO ⁺) | (3-CO ⁺) | Naphthalene <i>M</i> ⁺ |
|------------------|----------------------|----------------------|--------------------------------------|
| 113 | 3.1 | 4.2 | 4.1 |
| 111 | 1.0 | 1.7 | 1.2 |
| 102 ^a | 51 ^a | 51 ^a | 59 ^a |
| 98 | 6.7 | 7.1 | 7.7 |
| 88 | 4.9 | 5.8 | 5.3 |
| 86 | 10.2 | 10.9 | 10.0 |
| 78 ^a | 39 ^a | 35 ^a | 37 ^a |
| 76 | 29.1 | 27.5 | 29.2 |
| 63 ^b | 19.9 | 19.4 | 20.0 |
| 51 | 19.2 | 18.3 | 17.5 |
| 38 | 5.3 | 5.1 | 4.7 |
| 26 | 0.6 | 0.3 | 0.3 |

^a Ions produced unimolecularly and, therefore, may show values higher than 100. ^b m/z 63 (C_5H_3) includes a small component of ions formed by direct decomposition (<1%).

Table 2. CA spectra of $C_{14}H_{10}^{+}$ ions (m/z 178) derived from 5*H*-dibenzo[*a,d*]tropone (4⁺) and naphtho[*a*]tropone (5⁺) compared with diphenylacetylene, anthracene, and phenanthrene M^{+} . The intensities are defined as in Table 1

| [<i>m/z</i>] | (4-CO ⁺) | (5-CO ⁺) | Phenanthrene | Anthracene | Diphenylacetylene |
|------------------|----------------------|----------------------|------------------|------------------|-------------------|
| 163 ^a | 33 ^a | 37 ^a | 30 ^a | 26 ^a | 11 ^a |
| 151 ^a | 210 ^a | 196 ^a | 163 ^a | 131 ^a | 117 ^a |
| 138 ^a | 12 ^a | 15 ^a | 13 ^a | 12 ^a | 16 ^a |
| 126 ^a | 18 ^a | 27 ^a | 17 ^a | 18 ^a | 31 ^a |
| 122 | 6.8 | 6.8 | 4.5 | 4.2 | 3.6 |
| 112 | 8.5 | 8.8 | 6.3 | 6.0 | 6.9 |
| 101 | | | | | 9.5 ^b |
| 98 | 15.8 | 15.4 | 12.4 | 12.1 | 11.7 |
| 88 ^a | 12 ^c | 11.7 ^c | 9.6 ^a | 9.9 ^a | 11 ^a |
| 87 ^a | 18 ^a | 18 ^a | 16 ^a | 16 ^a | 14 ^a |
| 86 | 18.6 | 18.7 | 17.1 | 16.7 | 14.8 |
| 74 | 23.5 | 22.3 | 13.3 | 22.3 | 13.5 |
| 62 | 16.0 | 16.7 | 18.4 | 19.5 | 12.4 |
| 50 | 8.5 | 8.9 | 12.6 | 13.2 | 12.7 |
| 38 | 2.4 | 2.6 | 5.0 | 5.5 | 4.6 |
| 26 | 0.1 | 0.4 | 0.6 | 0.5 | 0.5 |

^a Ions which are produced unimolecularly and, therefore, may show values higher than 100. ^b m/z 101 loss of C_6H_5 radicals. ^c Unresolved peak.

are then discussed by comparison with the MNDO⁶ calculations.

Experimental Results

The EI spectra (80 eV) of tropone (1) and the benzoannulated homologues (2)–(5) are characterized by the specific loss of CO, analogous with substituted tropone derivatives.^{2,3a} The decarbonylation reaction constitutes the main process, which is preferred at reduced electron energy levels (nominally 18 eV). The resulting $M - CO^{+}$ ions were supposed to possess aromatic structures because of the identical fragmentation patterns when compared with the corresponding aromatic systems.^{2,3a} In order to justify this assumption we have analysed the structures of the $M - CO^{+}$ ions by collisional activation (CA)

Table 3. Results of the gas-phase pyrolysis g.c.-m.s. for the tropones (1)–(5) at 900 °C compared with the intensities of the M^{+} and $M - CO^{+}$ ions (EI 80 eV)

| Compound No. | Precursor | Product of pyrolysis (%) | Intensities (rel. %B) | |
|--------------|--|--------------------------------|-----------------------|----------------------------|
| | | | <i>M</i> ⁺ | <i>M - CO</i> ⁺ |
| (1) | Tropone | Benzene (100) | 38 | 100 |
| (2) | Benzo[<i>a</i>]tropone | Naphthalene (100) | 14.3 | 100 |
| (3) | Benzo[<i>a</i>]tropone | Naphthalene (100) | 20.3 | 100 |
| (4) | 5 <i>H</i> -Dibenzo[<i>a,d</i>]tropone | Phenanthrene (95) ^a | 54.5 | 100 |
| (5) | Naphtho[<i>a</i>]tropone | Anthracene (95) ^a | 14.1 | 100 |

^a In the pyrolysis, 5% of by-products are detected as decomposition products of the aromatic systems.

Table 4. Kinetic energy release T_x in eV (kJ mol⁻¹) at peak height x for the process $M^{+} \rightarrow M - CO^{+}$ for the tropone ions (1⁺)–(5⁺)

| <i>T</i> | (1 ⁺) | (2 ⁺) | (3 ⁺) | (4 ⁺) | (5 ⁺) |
|-------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| <i>T</i> _{0.1} | 872 (84.1) | | | | |
| <i>T</i> _{0.2} | 760 (73.3) | | | | |
| <i>T</i> _{0.5} | 565 (54.5) | 775 (74.8) | 714 (67.1) | 840 (81.1) | 840 (81.1) |
| <i>T</i> _{0.8} | 443 (42.7) | | | | |

mass spectroscopy. The results are summarized in Tables 1 and 2.

In most cases the CA data show almost identical values for the $M - CO^{+}$ ions and the respective aromatic compounds. Although absolute proof can only be given by demonstrating that non-aromatic ions of the same molecular composition have different spectra, the results strongly point towards aromatic structures of the $M - CO^{+}$ fragment ions. Thus, the tropone ion (1) yields $C_6H_6^{+}$, analogous with the qualitative analysis of the EI fragmentations^{2a,7} and the collisional-induced fragmentation pattern that has been published.⁸ The benzotropone ions (2⁺) and (3⁺) form the naphthalene system as it was assumed for the CO loss of the benzo[*a*]tropone ion (3⁺). However, the 5*H*-dibenzo[*a,d*]tropone ion (4⁺) and the naphtho[*a*]tropone ion (5⁺) decompose to $C_{14}H_{10}^{+}$ ions (m/z 178) with identical CA spectra (Tables 1 and 2), although the reaction products should be the phenanthrene (4-CO⁺) and anthracene (5-CO⁺) ions, respectively.^{7a,9a} This indicates that a mixture of interconverting ion structures is probably present, which differ from the model ion diphenylacetylene (M^{+} , loss of the C_6H_5 radical) and 9-methylenefluorene.^{9a}

For verification of the analogy of the thermal- and EI-induced decarbonylation of tropones it is useful to compare the CA results of the 'stable' (lifetime > 10⁻⁵ s) $M - CO^{+}$ ions with the products formed *via* gas-phase pyrolysis in combination with g.c.-m.s.⁵ The tropones (1)–(5) decompose quantitatively at 900 °C to the systems postulated,¹ summarized in Table 3. For example, dibenzotropone (4) yields phenanthrene as the main product, whereas naphtho[*a*]tropone (5) forms anthracene. The by-products detected by this method are the result of further decompositions of the aromatic structures being formed.⁵ Therefore comparable mechanisms can be assumed for the thermal and EI fragmentation processes, which afford rearrangements in accordance with Scheme 1. The translation energies released in the decarbonylation of the ionized tropones (1)–(5) are shown in Table 4.

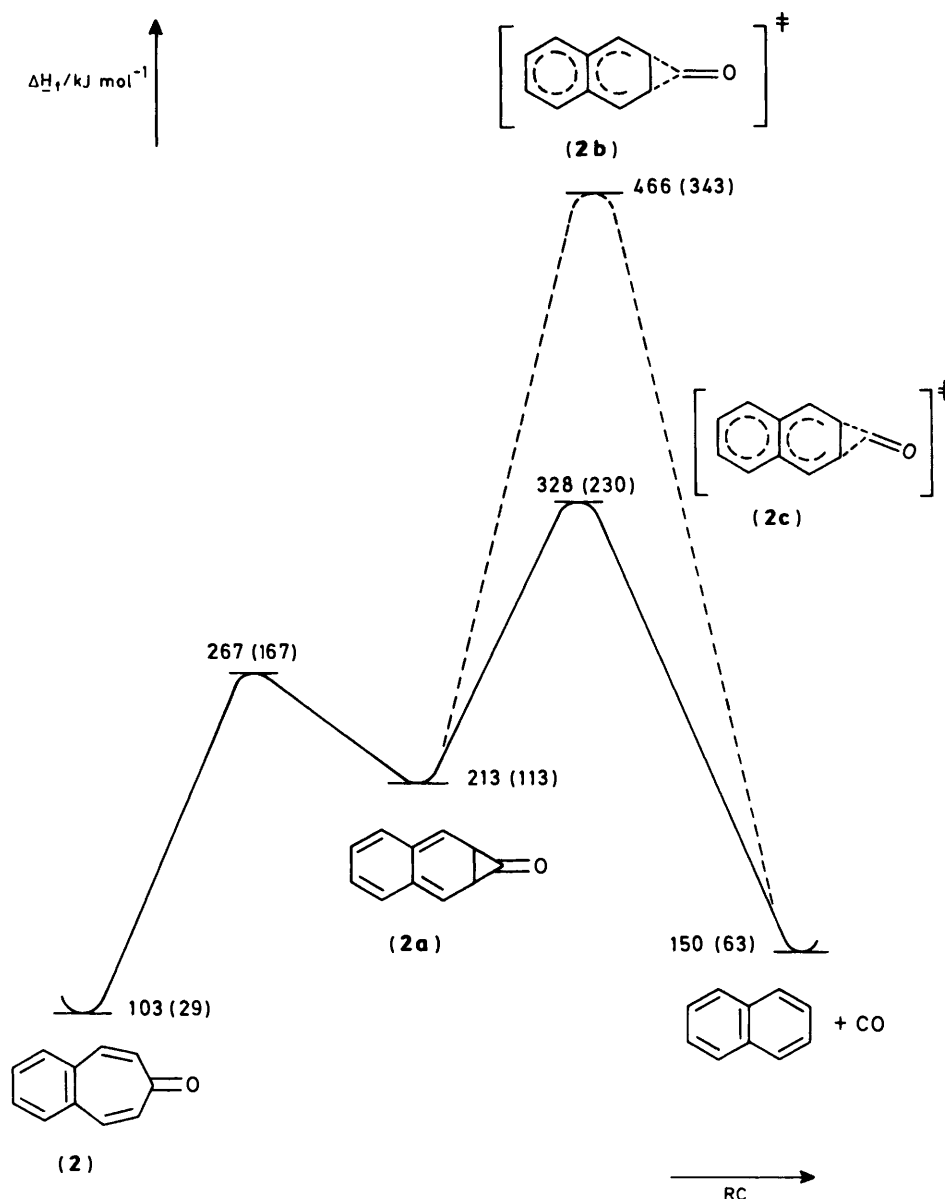


Figure 1. Calculated (MNDO) reaction profile for the CO elimination of benzo[*a*]tropone (2). The values for tropone (1) are given in parentheses. RC = reaction co-ordinate.

Calculated Results and Discussion

For detailed studies of the reaction mechanisms, we performed semiempirical SCF calculations using Dewar's MNDO method.⁶ For the calculated transition states, the gradient-search method was employed and the transient species were characterized by one negative eigenvalue of the force-constant matrix. The calculated reaction profiles for the neutral and cationic CO loss of (1) and (1⁺) and (2) and (2⁺) are shown in Figures 1 and 2, respectively.

For an assessment of the reliability of the calculated data it should be kept in mind that MNDO is a method with parameters for neutral molecules with a known accuracy.⁶ The employment of MNDO for the calculation of radical cations is a tentative approach, but previous work¹⁰ indicates that the results are reliable at least qualitatively, *i.e.*, relative stabilities of different structures are correctly reproduced.

As assumed for the thermal CO extrusion,¹ a sequence of symmetry-allowed processes is indicated,⁴ starting with the disrotatory ring closure to the norcaradienone intermediate

(a).^{1a,2b,3b} The rate-determining second step involves the cheletropic CO extrusion, which is, like the singlet carbene addition to olefines, symmetry allowed for the non-linear approach.^{4b} The calculated transition state for this reaction step is partially shown in Figure 3.

The unsymmetrical stretching of the C–C bonds and the 'inward' bending of the carbonyl group are very similar to the calculated transition state for carbene addition.¹¹ The symmetrical CO extrusion is much higher in energy as is shown in Figure 1.

In contrast to these results, the potential-energy profiles of the radical cations (Figure 2) show characteristic differences. We find that the calculated barriers for the ring closure are smaller for the cations in both cases. The opposite result holds true for the reverse reaction. Previous investigations of the correlation between ionic and neutral electrocyclic processes¹² gave no clear-cut picture concerning the stereochemical path of cationic ring-opening reactions. However, it was concluded from experimental^{12b,c} and theoretical results^{12a} that the effect

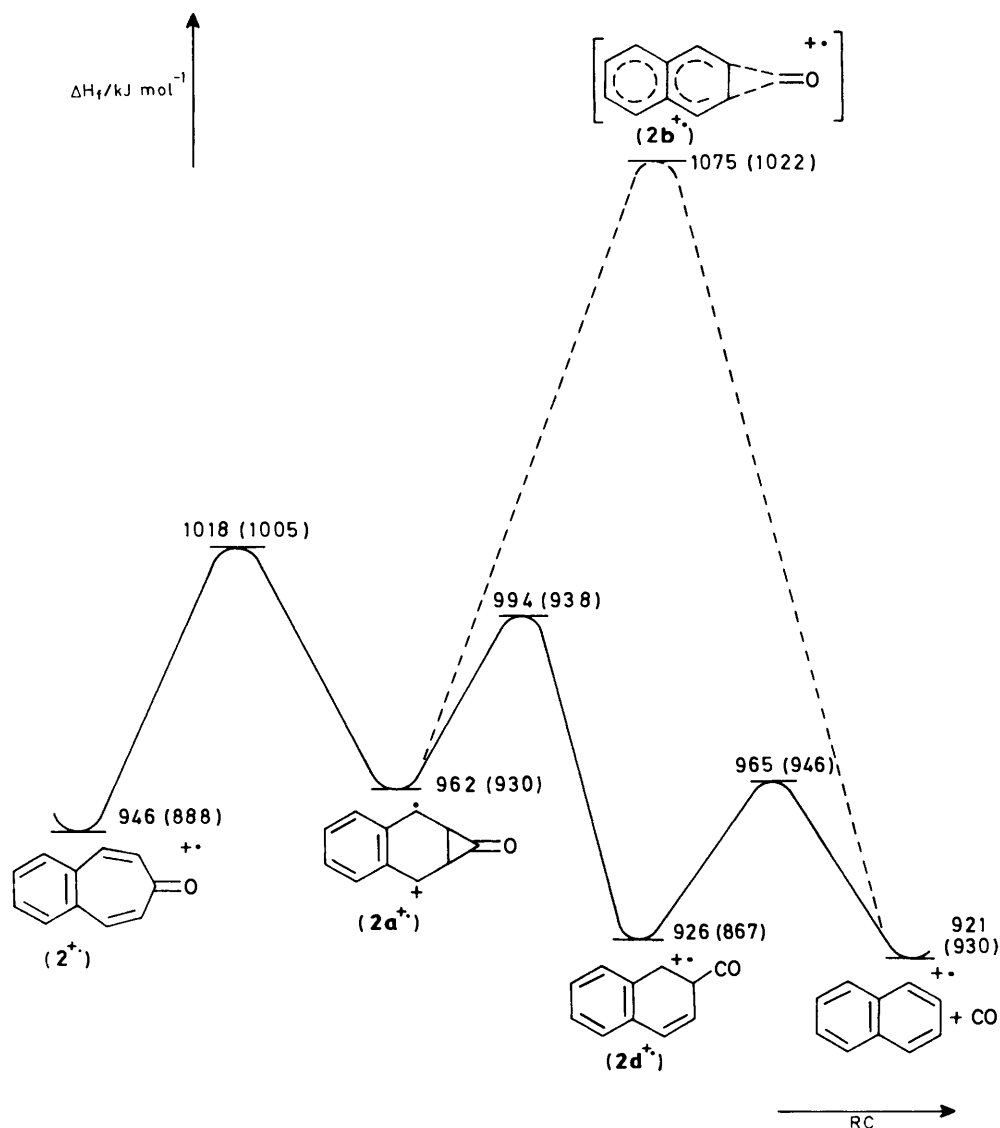


Figure 2. Calculated (MNDO) reaction profile for the CO elimination of the benzo[*a*]tropone ion (2^+). The values for the tropone ion (1^+) are given in parentheses

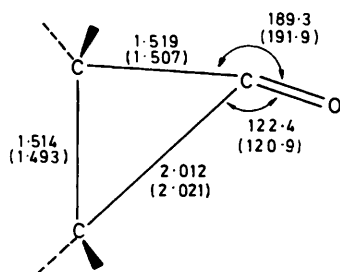


Figure 3. Part of the calculated transition state for the cheletropic CO elimination from benzo[*a*]tropone (**2**) [tropone (**1**)], structure (c) in Figure 1. Bond lengths in Å, bond angles in degree.

of ionization on the activation barrier for the ring-opening reaction of cationic cyclobutene is a lowering one. In our case, the ionic ring-opening reaction of both structures is calculated to be much more exothermic than the neutral reaction, which

may be the reason for the lower activation energy. Furthermore, the formation of the intermediate (a^+) is not only the rate-determining step, but it also reacts further to the more stable benzoyl-type ion (d^+), which is the actual precursor for the eventual CO elimination. Thus, the second step of the thermal reaction is, in the case for the cations, not characterized by a pericyclic mechanism, but is divided in two consecutive reaction steps. Again, calculation of a symmetrical CO loss from (a^+) via (b^+) shows a much higher energy transition state. There are differences in the thermodynamic course of (1^+) and (2^+): the benzene ion is formed endo-energetically, while the naphthalene cation is the result of an exo-energetic process (Figure 2).

More information can be obtained when the data for 4,5-benzotropone (**2**) and (2^+) are compared with tropone (**1**) and (1^+). For the neutral structures, the formation of the norcaradienone intermediate (**a**) (Figure 1) demands more activation energy (164–138 kJ mol⁻¹) and is thermodynamically less favoured (110–84 kJ mol⁻¹) for (**2**) than with (**1**). This is consistent with the loss of aromatic resonance energy as shown above for (**2a**). The resonance energy is regained in the second

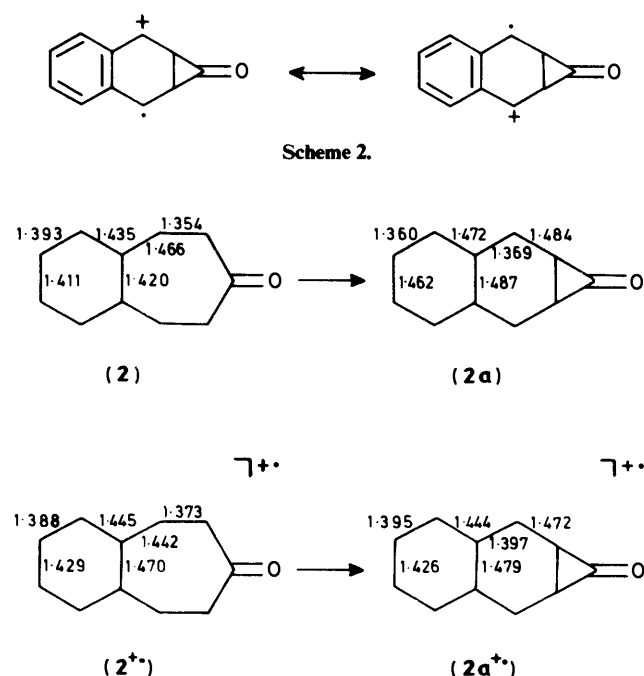


Figure 4. Part of the calculated bond lengths for structures (2), (2a), (2²⁺), and (2a²⁺) in Å

step; the difference (63–50 kJ mol⁻¹) reflects the larger aromatic system of naphthalene compared with benzene.

The situation is totally different for the radical cations. Here, the formation of the intermediate (a^{•+}) is kinetically (72–117 kJ mol⁻¹) and thermodynamically (16–42 kJ mol⁻¹) less demanding for the benzo[*a*]tropone cation (2^{•+}) than for (1^{•+}) (Figure 2). This can be explained when (2a^{•+}) is written down using valence bond structures as given in Scheme 2. Formation of (2a^{•+}) from (2^{•+}) does *not* enforce loss of aromatic stabilization, as in the case of the neutral structures. This model-like explanation is supported by the calculated changes in the C–C bond lengths of the aromatic ring for (2) and (2^{•+}) as shown in Figure 4.

While the formation of the neutral norcaradienone intermediate (2a) clearly involves bond alteration in the aromatic ring, there is hardly any distortion in the cation. Thus, the aromatic ring merely leads to a larger radical and charge delocalization resulting in an energetically more favoured reaction path. Finally, the CO extrusion from (2a^{•+}) *via* (d^{•+}) is exothermic by 63 kJ mol⁻¹, whereas the decarbonylation from (1a^{•+}) is energetically balanced. This is simply due to the higher ionization energy of benzene (9.25 eV) compared with naphthalene (8.15 eV).¹³

These conclusions agree with the experimentally determined values of the kinetic energy release shown in Table 4. The data show a significant larger translational energy release for the benzoannulated structures, which is consistent with the reaction profile shown in Figure 2.

Conclusions

The calculated reaction profiles shown in Figures 1 and 2 elucidate the different mechanisms of the thermal- and electron impact-induced decarbonylation and, furthermore, the differences in the reactions of tropone and benzoannulated tropones. The kinetics of the thermal processes are controlled by the cheletropic CO elimination *via* the unsymmetrical transition

state (c). The reaction course of the EI-induced reaction is controlled by the electrocyclic rearrangement to the norcaradienone intermediate (a^{•+}). While benzoannulation facilitates the reaction course kinetically and thermodynamically for the radical cations, decarbonylation becomes energetically more demanding for the benzoannulated neutral tropones. This can be explained by the differences in the calculated structures of intermediates (a) and (a^{•+}) compared with the neutral and cationic tropones, respectively.

Experimental

The tropones (1)–(5) were synthesized following literature procedures: tropone (1),¹⁴ benzo[*a*]tropone (2),¹⁵ benzo[*a*]tropone (3),^{15b,c,16} 5*H*-dibenzo[*a,d*]tropone (4),¹⁷ and naphtho[*a*]tropone (5).¹⁸ The structures of the compounds were verified by spectroscopic methods.

The EI spectra were obtained with a Varian MAT 711 double-focusing mass spectrometer under the following general conditions: water-cooled direct inlet system; source temperature 150 °C; accelerating voltage 8 000 V; emission current 0.8 mA; electron energy 80 eV; and mass resolution $R = 2\,000$ (10% valley definition). The low ionization energy experiments were performed using the same instrument. The exact mass measurements were employed at resolution 12.000 (10% valley definition; peak-matching method). The measurements of the metastable ions were obtained by applying the method of varying the accelerating voltage keeping the electric and magnetic field constant and by recording the metastable peak shapes with the SS 100 data system.

The CA spectra within the second field-free region were determined on a CH 5-DF mass spectrometer (Varian MAT) with 'reversed' Nier-Johnson-geometry. The instrument conditions were: accelerating voltage 3 000 V; emission current 0.3 mA; electron energy 80 eV; air as target gas at 10⁻⁵ Torr.

The gas-phase pyrolysis in combination with g.c.–m.s. is described elsewhere.⁵

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