Figure 6. ESR spectra of **16**[•−] and **16**[•3−]: solvent, DME; temperature, 273 K (**16**[•−]) and 233 K (**16**[•3−]). All values in mT. From ref 14.

The third half-wave reduction potentials, $E_{1/2}^{(3)}$, which are relevant to the ease of formation of the radical trianions, have been estimated as −3.23 V (vs. SCE) for both **14** and **15** and as −2.60 V for **16**.[14] Although a substantially less negative $E_{1/2}^{(3)}$ value of −2.06 V[56]

is indicated by the cyclic voltammogram of the recently synthesized tetracyano-9,10-anthraquinodimethane (**17**),[56,57] attempts to observe the ESR spectrum of **17**[•3−] have failed because of the low kinetic stability (persistence) of this radical trianion.[56]

Concluding Remarks

The occurrence of π-radical trianions, which can be both detected and characterized by ESR and ENDOR spectroscopy, widens the research area of paramagnetic organic molecules. Despite their high negative charge, it is possible to interpret the structure of these radical trianions by the same simple π-MO models as those used for the radical anions. Since the singly occupied orbitals in the radical anion and in the corresponding radical trianion differ in their nodal properties, the major π-spin populations in the two species reside not only on different atoms but also frequently in different regions of the molecular framework. Due to this dissimilar π-spin distribution, the differences in the physical and chemical behavior of the radical anions and the radical trianions should go beyond those expected on grounds of the unequal charges. One is therefore justified in considering the radical trianions as new molecular species, of which only a relatively small number has hitherto been investigated. The surface of this research area has hardly been scratched, but the list of known radical trianions is steadily growing and will do so in the near future.

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Hydrocarbon Radical Cations

JOHN L. COURTNEIDGE and ALWYN G. DAVIES*

Chemistry Department, University College London, London WC1H OAJ, U.K.

Introduction

In 1980, the hydrocarbon radical ions which were then known were indexed in Landolt Börnstein. The radical anions occupied 149 pages,[1] but the radical cations occupied only 15 pages,[2] a ratio of 10 to 1.

John Courtneidge was born in London in 1951. He graduated from the University of Bristol, and after a period teaching chemistry in London schools he completed, in 1981, his Ph.D. at University College London (with A. J. Bloodworth). Since then he has worked at UCL with Professor Davies. He is presently developing a career in commercial horticulture.

Alwyn Davies was born in 1926. He obtained his B.Sc. and Ph.D. degrees at University College London with C. K. Ingold; then after a period as Lecturer at Battersea Polytechnic with J. Kenyon, he returned at UCL in 1953. His research has included studies of organic peroxides, of organometallic compounds, and of free radical reactions.

Yet one can argue that, from both theoretical and experimental viewpoints, this is in inverse ratio to their relative importance.

First (Figure 1), the SOMO of the radical cation corresponds with the HOMO of the parent, and the best way of investigating the electron distribution in RH is to examine the ESR spectrum of RH[•+].

Second, the radical ions, like the electronically excited states, provide a readily accessible and reactive elec-

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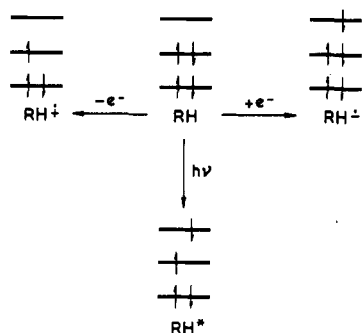
Figure 1. Orbital occupancy in RH, RH$^{\bullet+}$, RH$^{\bullet-}$, and RH*.
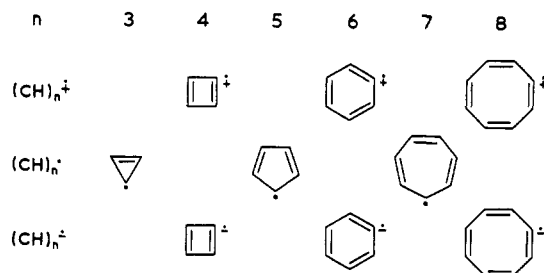

Figure 2. Odd annulene radicals and even annulene radical ions.

tronic modification of RH, with an important potential in organic synthesis. Whereas the special reactivity of the photoexcited states has already been exploited extensively, that of the radical ions has received little attention. It seems likely that the major developments which are taking place in synthetic methods involving neutral radicals will soon be accompanied by similar developments involving the use of radical ions, and present indications are that, at least in cycloaddition processes, the reactions of the radical cations will prove to be more useful than those of the radical anions.[3]

Since 1980, this imbalance in our understanding of the radical anions and cations has been redressed to some degree. A number of groups of workers have exploited the discovery that radical cations can be generated by γ-radiolysis of a dilute solution of a solute in a frozen Freon matrix.[4,5] Keeping one eye on the potential in organic synthesis, we have been carrying out complementary ESR studies of the generation, nuclear and electronic structures, and reactions of hydrocarbon radical cations in fluid solution, and some of our results with simple alkenes and alkynes are reviewed here.
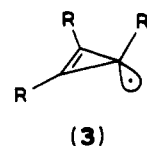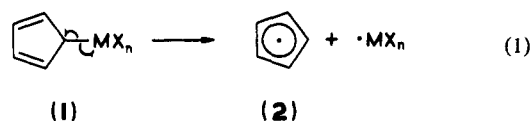
Cyclobutadiene Radical Cations

We were led into this field by our previous work on cyclopentadienyl radicals.

The odd annulenes $(CH)_n$ (n odd) and the monoions derived from the even annulenes (Figure 2) contain an odd number of electrons and can be studied by ESR spectroscopy.

We had found that the cyclopentadienyl ([5]-annulene) radicals could be generated in fluid solution by the photolytic homolysis of the carbon–metal bond in cyclopentadienylmetallic compounds (1) (eq 1), and we[6–11] and Sakurai[12,13] had thoroughly studied their

electron distributions by ESR spectroscopy. This showed them to be π-delocalized (2) like benzene ([6]annulene) itself, but unlike the cyclopropenyl ([3]annulene) radicals which have a σ-configuration (3).[14,15]
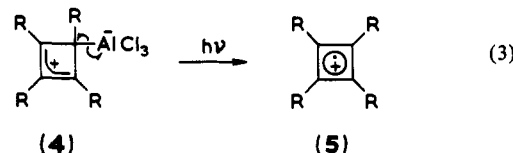

By 1981, derivatives of all the annulenes shown in Figure 2 were known except $C_4H_4^{\bullet+}$ and $C_4H_4^{\bullet-}$, and we were eager to extend our studies to these species which might represent the smallest π-delocalized annulenes.

The first cyclobutadiene radical cation was detected by ESR spectroscopy in 1981. Bock, Roth, and Maier treated tetra-*tert*-butylcyclobutadiene or tetra-*tert*-butyltetrahedrane with aluminum chloride in dichloromethane and observed a strong ESR spectrum of the tetra-*tert*-butylcyclobutadiene radical cation.[16]
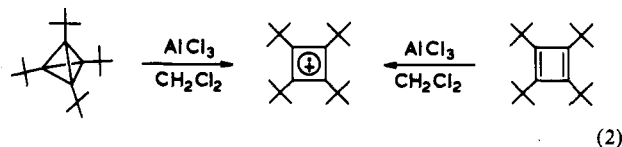
A more general method was established by Broxterman, Hogeveen, and Kok.[17]   2-Butyne reacts with aluminum chloride in dichloromethane to give the σ-complex of tetramethylcyclobutadiene and $AlCl_3$ (4; R = Me).[18,19] Such compounds are analogous to the cyclopentadienyl derivatives (1); they have a similar fluxional structure, and they similarly undergo photolysis to generate the corresponding annulene radical, which in the present case is the tetramethylcyclobutadiene radical cation (5; R = Me).[17]

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Figure 3. ESR spectra from (a and b) Me-t-BuC$_2$ and (c) Me$_2$C$_2$ + t-Bu$_2$C$_2$. The signals are assigned as follows: A, *cis*-Me$_2$-t-Bu$_2$C$_4$$^{•+}$; B, *trans*-Me$_2$-$t$-Bu$_2C_4$$^{•+}$; C, Me$_4C_4$$^{•+}$, and t-Bu$_4C_4$$^{•+}$. Note the differences between the g values, which is obvious in (c).[25]

This method is still restricted in that complexes similar to (4) can be prepared only when R is a primary alkyl group.[20-23]

We simplified and generalized this procedure by merely photolyzing a mixture of the alkyne and aluminum chloride in dichloromethane at low temperature

(eq 6).[23-26] This method is successful even when the AlCl$_3$ complexes cannot be prepared, and also, by the judicious use of mixed alkynes or of mixtures of a simple and/or a mixed alkyne, cyclobutadiene radical cations containing mixed alkyl groups can be generated (eq 4-7). The superimposed spectra of *cis*- and *trans*-Me$_2$-t-Bu$_2$C$_4$$^{•+}$, which are obtained from the reaction of methyl-*tert*-butylacetylene, are shown in Figure 3.[25]

$$2 \; R{-}{\equiv}{-}R \xrightarrow[h\nu]{AlCl_3 \; CH_2Cl_2} \text{(structure)} \qquad (4)$$

$$\begin{array}{c} R{-}{\equiv}{-}R \\ R'{-}{\equiv}{-}R' \end{array} \longrightarrow \text{(structure)} + R_4C_4^{•+} + R_4'C_4^{•+} \qquad (5)$$

$$2 \; R{-}{\equiv}{-}R' \longrightarrow \text{(structures)} \qquad (6)$$

$$\begin{array}{c} R{-}{\equiv}{-}R \\ R{-}{\equiv}{-}R' \end{array} \longrightarrow \text{(structure)} + R_4C_4^{•+} + \textit{cis-} \text{ and } \textit{trans-}R_2R_2'C_4^{•+} \qquad (7)$$

We thought initially that we were imitating Hogeveen's synthesis, our reactions proceeding through the intermediate formation of the σ-complexes (4), in too low concentrations to be detected, but this is not necessarily so. If but-2-yne is γ-irradiated in a rigid Freon matrix at 77 K, the alkyne radical cation is formed. If the matrix is then allowed to warm and soften so that the solute molecules can migrate, the radical cation reacts with the parent alkyne, and the ESR spectrum of the cyclobutanediene radical cation becomes apparent (eq 8).[27,28]

$$\begin{array}{c} Me{-}{\overset{•+}{\equiv}}{-}Me \\ Me{-}{\equiv}{-}Me \end{array} \longrightarrow \text{(structure)} \qquad (8)$$

If the same experiment is performed with deca-2,8-diyne, the spectrum of the cyclobutadiene radical cation (6) can be observed at 77 K without annealing: the reaction of the radical cation with the alkyne is now intramolecular and requires only rotational rather than translational motion before it can take place (eq 9).[27]

$$\text{(structure)} \xrightarrow{\gamma} \text{(structure)} \longrightarrow \text{(structure)}$$

(6)
$$(9)$$

The generation of the tetramethylcyclobutadiene radical cation by the electrolysis of but-2-yne probably represents a further example of reaction 8.[22]

By reaction 3, and particularly by reactions 4-7, a large number of tetraalkylcyclobutadiene radical cations have been generated and identified in solution by ESR spectroscopy.[17,20-27] Despite their short history, they already constitute the family of hydrocarbon radical cations for which the relation between spectra and

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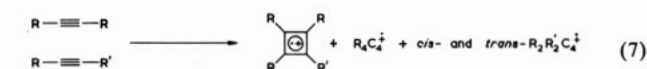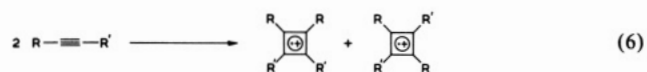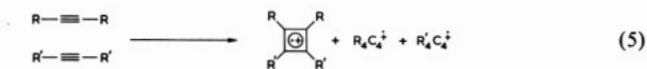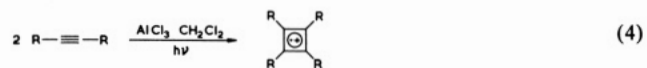(22) Broxterman, Q. B. Thesis, Groningen, 1985.
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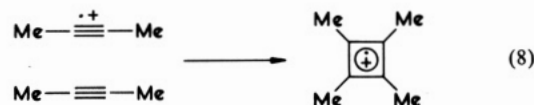(24) Courtneidge, J. L.; Davies, A. G.; Parkin, J. E. *J. Chem. Soc., Chem. Commun.* **1984**, 1262.
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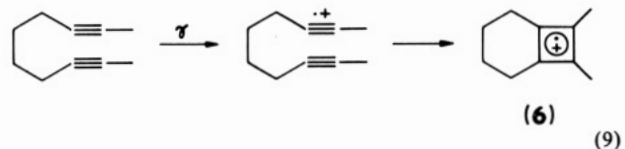
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	Hyperfine coupling constant / G			g	Ref.
	Hβ	Hγ	^{13}Cα		
Me$_4$C$_4^+$	8.70 (12H)		4.04	2.0030	17,25
(MeCH$_2$)$_4$C$_4^+$	7.99 (8H)		5.00	2.0029	25
(EtCH$_2$)$_4$C$_4^+$	7.15 (8H)			2.0029	25
(Pr^{i}CH$_2$)$_4$C$_4^+$	6.5 (8H)			2.0027	25
(Bu^{t}CH$_2$)$_4$C$_4^+$	4.32 (8H)			2.0026	21,22
Pr$^i_4$C$_4^+$	2.76 (4H)	0.28 (24H)		2.0027	25
Bu$^t_4$C$_4^+$		0.27 (36H)	10	2.0022	8,16
1-Ad$_4$C$_4^+$		-0.14 (12 H)	10.76^a	2.0021	26
cis-Me$_2$Bu$^t_2$C$_4^+$	8.00 (6H)	0.24 (18H)	4.0	2.0028	25
trans-Me$_2$Bu$^t_2$C$_4^+$	9.00 (6H)		4.0	2.0028	25
cis-Et$_2$Bu$^t_2$C$_4^+$	4.45 (4H)	0.20 (18H)		2.0028	24,25
trans-Et$_2$Bu$^t_2$C$_4^+$	4.31 (4H)	0.20 (18H)		2.0028	24,25
(CH$_2$)$_5$ C$_4$ (CH$_2$)$_5$$^+$	5.4 (4H$_{eq}$) 16.2 (4H$_{ax}$)	ca.0.35		2.0030	21

^{a} $a(24 H\delta) = +0.28$ G, $a(^{13}C\beta) = a(^{13}C\gamma) = 3.0$ G

structures has been most thoroughly investigated, and many more of the cyclobutadiene radical cations than of the parent cyclobutadienes have been observed directly. The ESR parameters of a selection of typical cyclobutadiene radical cations are given in Table I.

Steric and Electronic Effects. The primary problem to settle is whether the cyclobutadiene radical cations have a π-configuration like the cyclopentadienyl radicals or an equilibrating σ-configuration (7) like the cyclopropenyl radicals. This can be determined from the magnitude of the hyperfine coupling by the ^{13}C atoms of the ring, which will be low, and approximately calculable, for a π-radical or relatively high for a σ-radical.

In the radical cations R$_4$C$_4^{•+}$, when R is a primary alkyl group such as CH$_3$CH$_2$, three sets of ^{13}C satellites can be observed with $a(^{13}C)$ between 4 and 5 G, relating to the C$_\alpha$ (ring), C$_\beta$, and C$_\gamma$ atoms, and the g value is about 2.0030.^{20} One of these satellite pairs broadens at low temperature, and as the bulk of the alkyl groups R increases, the hyperfine coupling constant for this particular pair increases to a limit of about 10 G when R = 1-adamantyl; and as the hyperfine coupling constant increases, so the g value decreases, to 2.0021 in 1-Ad$_4$C$_4^{•+}$.^{26}

(7) **(8)** **(9)**
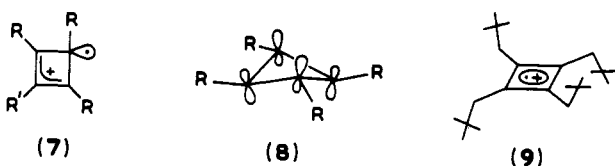
This suggests that these satellites relate to the ^{13}C atoms of the ring: when the alkyl groups are small, the ring is planar and the electrons are π-delocalized. In the smaller cyclopropenyl radicals (3), such delocalization may be inhibited by the larger ring strain which would be involved if an sp^2 hybridized radical center were to be incorporated into the ring.^{22,25}

When the alkyl groups are bulky, their steric interaction can be relieved by ring puckering, as illustrated in (8), which introduces some σ-character into the SOMO, with an increase in $a(^{13}C_\alpha)$. The value of $a(^{13}C)$ of ca. 5 G is close to that calculated for a π-radical, and the presence of steric strain when R is large, which can be relieved by ring puckering, is confirmed by molecular mechanics calculations.^{29}

Steric and electronic effects can also be identified which relate to the conformation about the ring–alkyl bond. In neutral radicals, hyperfine coupling to hydrogen on the β-carbon atoms is described by eq 10,

$$a(H_\beta) = \rho_{C_\alpha}(A + B \cos^2 \theta) \tag{10}$$

where ρ_{C_α} is the spin density on C$_\alpha$ and θ is the dihedral angle between the C–H bond and the axis of the singly occupied 2p orbital; A (ca. 1 G) and B (ca. 54 G) are constants which relate to the mechanisms of spin polarization and of hyperconjugation, respectively.

As expected, an equation of similar form appears to govern hyperfine coupling in radical cations. In the series (RCH$_2$)$_4$C$_4^{•+}$, R = H, Me, Et, i-Pr, and t-Bu (see Table I), the value of $a(H_\beta)$ drops progressively from 8.70 to 4.30 G. This implies that as the bulk of R increases, the groups R are increasingly forced into a position orthogonal to the plane of the ring (e.g., 9).

Molecular mechanisms (MM2) calculations have been used to rationalize the low values of $a(H_\beta)$ which are observed in the cis and trans isomers of Et$_2$-t-Bu$_2$C$_4^{•+}$, and they confirm that conformations with a large CH dihedral angle θ, such as 10, are strongly favored.^{24,29} Similar calculations can account for the different hyperfine coupling constants to axial and equatorial H$_\beta$ atoms which are observed in tricyclic compounds such as 11.^{29,30}

(10) **(11)** **(12)**
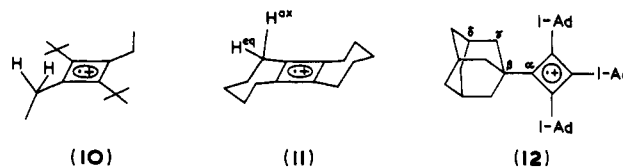
From the data at present available, it appears that the values of A and B in eq 12 will lie in the range +5 to +9 G and +55 to +60 G, respectively, for radical cations, resulting in rather larger values for $a(H_\beta)$ than are observed in neutral radicals.^{29,30}

The spectrum of the tetra-1-adamantylcyclobutadiene radical cation (12) is particularly interesting. Selective deuteriation shows that $a(H_\delta)$ (+0.28 G) is double $a(H_\gamma)$ (-0.14 G). Perdeuteriation reveals a family of ^{13}C satellites which are unusually intense because of the large number of equivalent carbon atoms. This satellite pattern can be analyzed by the use of probability theory, and for the first time ^{13}C satellites of ^{13}C satellites can be identified in a hydrocarbon radical ion.^{26}

The model based on the breaking of orbital degeneracy has been used extensively to analyze the electronic effects of substituents in benzene radical anions and cations and in cyclopentadienyl radicals.$^{6-13}$ If this model is applied to the analysis of the relative electronic effects of the alkyl groups in cis- and trans-Me$_2$-t-Bu$_2$C$_4^{•+}$, it leads to the conclusion that tert-butyl groups are more electron releasing than methyl groups in this environment. There are some inconsistencies in this model, however, and it may be that the electronic effects are obscured by other effects such as solvation or counterion interaction or in-plane distortion of the ring.^{25,29}

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Azulene Radical Cations

Whereas dialkylacetylenes react with aluminum chloride to give cyclobutadiene radical cations, arylacetylenes under the same conditions are converted into tars, and no ESR spectra can be observed. However, if diaryl- or alkylarylacetylenes are photolyzed in trifluoroacetic acid containing mercury(II) trifluoroacetate (a reagent first used by J. Kochi[31]), strong, complex, stable spectra are observed, and analysis of these by ENDOR spectroscopy shows that they result from too many nonequivalent proton interactions for them to be associated with the monomeric acetylenes or their derived cyclobutadienes.[32]

By isolation of the products, the spectra were shown to result from the formation of azulenes; for example, diphenylacetylene gives the 1,2,3-triphenylazulene radical cation (13; R = Ph), and methylphenylacetylene gives the unsymmetrically substituted 1,2-dimethyl-3-phenylazulene (13; R = Me).

This remarkable expansion of the benzene ring is recognized to occur in isolation during mass spectrometry,[33] and the overall rearrangement and dimerization to give an azulene are known to take place with a variety of Lewis acids.[34-37] The sequence in which the oxidation, the rearrangement, and the dimerization occur is not known, but one of a number of possibilities is shown in eq 11.

(11)
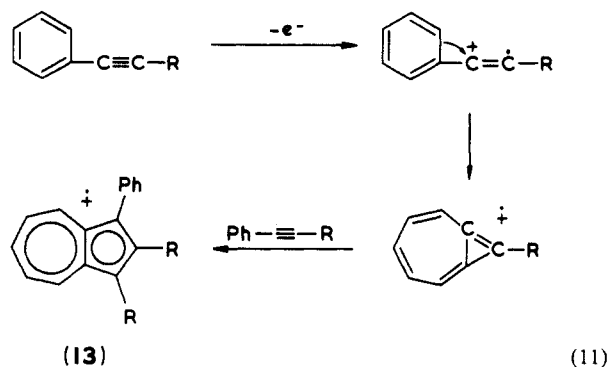
Dialkyl- and Diaryldiacetylene Radical Cations

With the dialkylacetylenes giving cyclobutadiene radical cations and the diarylacetylenes giving azulene radical cations, a variety of modes of behavior might be envisaged for the dialkyl- and diaryldiacetylenes. In fact, the dialkyldiacetylenes appear to be free of any complication, and in the presence of Kochi's reagent they give rise to spectra of the monomeric unrearranged radical cations (eq 12), despite the fact that the degeneracy of the $2p_x$ and $2p_y$ orbitals in the parent diynes might be expected to lead to severe line broadening.[38]

$$R{-}{\equiv}{-}{\equiv}{-}R \quad \xrightarrow{-e^-} \quad R{-}{\equiv}{-}{\equiv}{-}R^{\cdot+} \qquad (12)$$

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Table II.
ESR Spectra of Radical Cations and Anions of Dialkyldiacetylenes, Diaryldiacetylenes, Diarylacetylenes, and Diarylethylenes

	Hyperfine coupling constant / G				*g*
MeC≡C-C≡CMe⁺	8.00 (6H)				1.9997
Me₃CC≡C-C≡CCMe₃	0.61 (18H)				1.9998
Me₃CC≡C-C≡CCMe₃	<0.1				1.9830
Ph-C≡C-C≡C-Ph ⁺	2.34 (4Ho)	0.70 (4Hm)	3.20 (4Hp)		2.0013
Ph-C≡C-C≡C-Ph ⁻	2.47 (4Ho)	0.67 (4Hm)	3.96 (2Hp)		2.0022
Ph-C≡C-Ph ⁺	2.22 (4Ho)	0.75 (4Hm)	3.14 (2Hp)		2.0024
Ph-C≡C-Ph ⁻	2.71 (4Ho)	0.59 (4Hm)	4.85 (2Hp)		2.0025
Me-C₆H₄-C≡C-C₆H₄-Me ⁺	3.375 (4Ho)	1.00 (4Hm)	5.75 (6H)		2.0025
Me-C₆H₄-C≡C-C₆H₄-Me ⁻	3.75 (4Ho)	0.92 (4Hm)	4.23 (6H)		
Ph-CH=CH-Ph ⁺	2.78 (4Ho)	0.715 (4Hm)	4.35 (2H) / 4.35 (2Hp)		
Ph-CH=CH-Ph ⁻	1.94 (2Ho) / 3.03 (2Ho)	0.30 (2Hm) / 0.83 (2Hm)	4.51 (2H) / 4.00 (2Hp)		

When R = Ph, the spectrum of the radical cation shows the presence of ^{199}Hg satellites, but otherwise it appears to be interpretable in terms of hyperfine coupling by the protons of two equivalent phenyl groups.

In Table II the ESR parameters of the radical cations are compared with those of the known di-*tert*-butyldiacetylene radical anion.[39] It will be seen that in both the radial anions and cations the *g* values are all low, lower than for free spin; presumably this arises from spin–orbit coupling between the near-degenerate $2p_x$ and $2p_y$ orbitals.

Diarylacetylene and Diarylethylene Radical Cations

Under milder conditions than those which convert diarylacetylenes into azulenes, spectra which appear to relate to the monomeric diarylacetylene radical cations can be observed (eq 13).

$$Ar{-}{\equiv}{-}Ar \quad \xrightarrow[h\nu]{CF_3CO_2H} \quad Ar{-}{\equiv}{-}Ar^{\cdot+} \qquad (13)$$
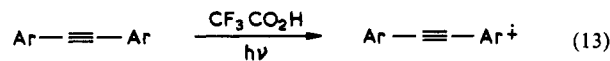
For example, careful photolysis of diphenylacetylene in trifluoroacetic acid shows a spectrum which, if it is recorded under the conditions when the lines are broad, is the same as the spectrum obtained by γ-radiolysis of diphenylacetylene in $CFCl_3$.[40]

In Table II, the ESR parameters of the diphenyl- and di-*p*-tolylacetylene radical cations are compared with those of the corresponding radical anions.

The radical cations of *trans*-stilbenes have been obtained by photolysis of either *cis*- or *trans*-stilbenes in

(39) Evans, A. G.; Evans, J. C.; Bevan, C. *J. Chem. Soc., Perkin Trans.* 2 **1974**, 1220.

(40) Chandra, H.; Courtneidge, J. L.; Davies, A. G.; Gregory, P. S.; Symons, M. C. R., unpublished work.

(41) Courtneidge, J. L.; Davies, A. G. *J. Chem. Soc., Chem. Commun.* **1984**, 136; unpublished work.

the presence of Kochi's reagent.[38] Rotation about the Ph–C bonds is fast on the ESR time scale, whereas in the corresponding radical anions it is relatively slow and nonequivalent ortho- and meta-hydrogen atoms can be distinguished (see Table II).
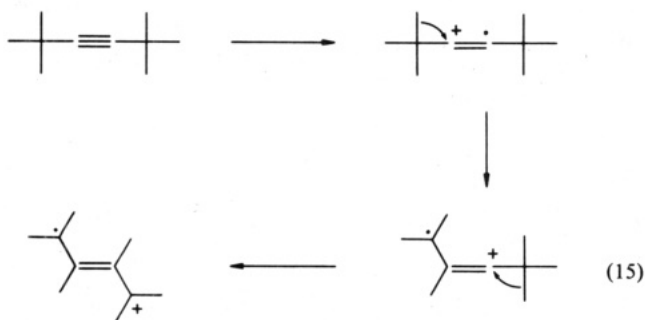
Butadiene Radical Cations

In the generation of tetra-*tert*-alkylcyclobutadiene radical cations from the alkyne and aluminum chloride by eq 4, the ESR spectrum of a different radical can sometimes be observed before the solution is photolyzed. When the solution is irradiated, the initial spectrum is rapidly lost and that of the cyclobutadiene radical cation appears.

These initial spectra relate to the radical cations of the hexaalkylbutadienes which can be formed by rearrangement of the di-*tert*-alkylalkynes, and the same spectra can be generated directly from the hexaalkylbutadienes (e.g., eq 14).[41]

$$(14)$$
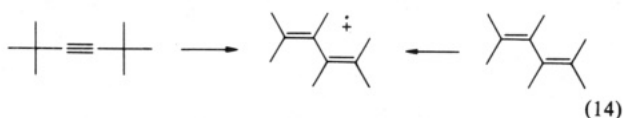
The rearrangement of di-*tert*-butylacetylene to hexamethylbutadiene has been observed previously to occur in superacids.[42] In common with the reaction of diarylacetylenes to give ultimately azulenes, it presumably involves a cationic intermediate, though whether this is a simple cation or a radical cation is not clear. One possible mechanism involving a radical cation, which has not been considered previously, but which illustrates the analogy with reaction 11, is illustrated in eq 15.

$$(15)$$

Other less highly alkylated butadiene radical cations (e.g., $Me_2C=CHCH=CMe_2^{\bullet+}$) can similarly be prepared by treating the diene with aluminum chloride in dichloromethane.[43]

Cyclopentadiene Radical Cations

Our accidental detection of the first ESR spectra of the alkylbutadiene radical cations prompted us to return to the alkylcyclopentadienes from which we had generated alkylcyclopentadienyl radicals. We had found that a strong spectrum of the pentamethylcyclopentadienyl radical could be observed when pentamethylcyclopentadiene was irradiated with UV light.[7,11] As radical cations can often be regarded as the conjugate acids of neutral radicals, it seemed possible that photolysis of pentamethylcyclopentadiene under acid conditions might provide a route to the penta-

Figure 4. ESR spectrum of the pentamethylcyclopentadiene radical cation in trifluoroacetic acid at −14 °C.[44]

Table III.
ESR Spectra of Radical Cations Derived from Butadienes and Cyclopentadienes

	Hyperfine coupling constants / G			
	σ(1,4)	σ(2,3)	σ(5)	g
	10.55 (2Me) 10.7 (2Me)	4.2 (2Me)		2.0028
	12.90 (2Me) 10.75 (2Me)	3.00 (2H)		2.0028
	14.4 (2Me)	4.0 (2Me)	1.3 (2Me)	2.0024
	15.0 (2Me)	4.0 (2Me)	0.8 (1Me) 1.6 (1H)	2.0027
	15.2 (2Me)	4.0 (2Me)	1.4 (2H)	

methylcyclopentadiene radical cation (14) by reaction 16.

$$(16)$$

$$(14)$$

Indeed, photolysis of pentamethylcyclopentadiene in trifluoroacetic acid does generate a strong ESR spectrum of the radical cation (14), as shown in Figure 4,[44] but the fact that similar behavior is found for hexamethylcyclopentadiene which does not yield a radical under neutral conditions[45] suggests that the mechanism in eq 16 may not be correct. In the same way the radical cation has been generated from tetramethyl- and trimethylcyclopentadiene.[43] The hyperfine coupling

(42) Olah, G. A.; Mayr, H. *J. Am. Chem. Soc.* **1976**, *98*, 7333.
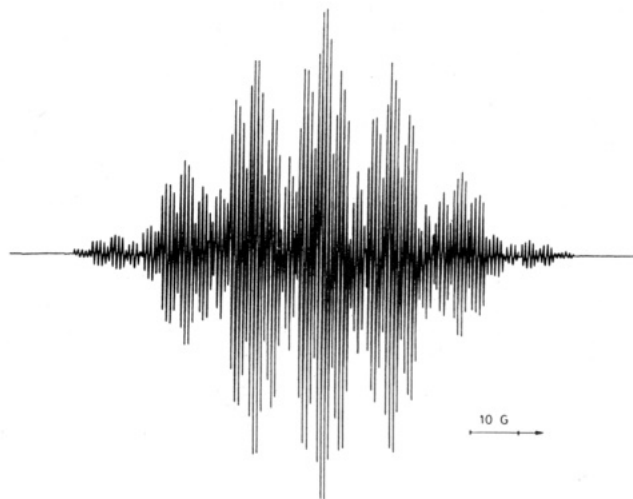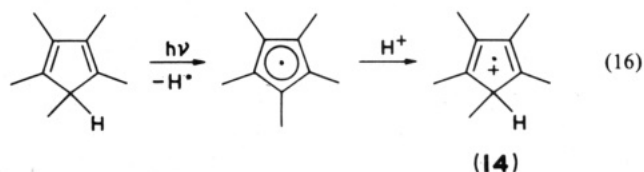(43) Courtneidge, J. L.; Davies, A. G.; Yazdi, S. N., unpublished work.
(44) Courtneidge, J. L.; Davies, A. G.; Yazdi, S. N. *J. Chem. Soc., Chem. Commun.* **1984**, 570.
(45) Courtneidge, J. L.; Davies, A. G.; Djap, D. H.; Gregory, P. S.; Yazdi, S. N. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 49.
(46) Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718.

constants (Table III) for substituents on the butadiene unit are consistent with those observed for the acyclic butadienes, but groups attached to the sp^3-hybridized carbon atom, which lies in the nodal plane of the diene π-system, show only a small hyperfine interaction.

A variety of other hydrocarbons such as anthracene, pyrene, di-*tert*-alkylacetylenes, and the diarylacetylenes referred to above, yield radical cations on photolysis in trifluoroacetic acid, and the mechanisms of these reactions are not yet clear. They appear not to depend on the presence of aerobic oxygen, nor to involve primary photoexcitation of trifluoroacetic acid. At the time of writing, photoinduced electron transfer from the hydrocarbon to trifluoroacetic acid or photoinduced CH bond homolysis in the protonated hydrocarbon seems to be the most likely mechanism.

Cyclohexadiene Radical Cations

These species have attracted much attention since Bauld showed in 1981 that the Diels–Alder dimerization of cyclohexa-1,3-diene was catalyzed by tris(4-bromophenyl)aminium hexachloroantimonate, $(BrC_6H_4)_3N^{\bullet+}SbCl_6^-$, when the reaction apparently involved the diene radical cation acting as the dienophile.

As yet, we have not been able to observe the monomeric radical cations in fluid solution, though they are familiar in Freon matrices.[47,48] The type of behavior which is observed is illustrated by 1,4-dimethylcyclohexa-1,3-diene (15). If this is treated with the aminium salt in dichloromethane, an ESR spectrum is observed which we ascribe to the tricyclic 1,5-diene (17), but if 2,6-di-*tert*-butylpyridine is present, *p*-xylene and not the dimer is formed.[49]

It seems that the radical cation of the parent diene is first formed, but it rapidly loses a proton which catalyzes the rearrangement of the diene. Of the possible isomers which can be formed, 16 has the least hindered double bond to serve as a dienophile, and a rapid cycloaddition occurs between 15 and 16$^{\bullet+}$ to give 17.
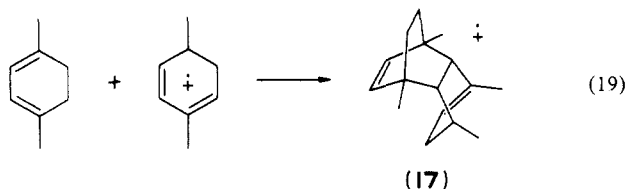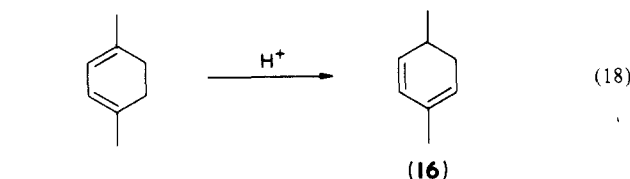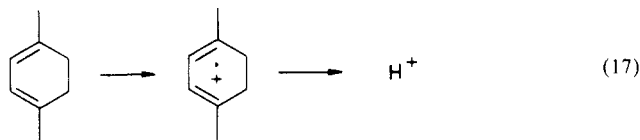
(17)

(15)

(18)

(16)

(19)

(17)

When a base is present to scavenge the proton, reaction 20 does not take place and no dimer is formed. The spectrum of the same radical cation (17) is observed when 1,4-dimethylcyclohexa-1,4-diene (18) is treated with tris(2,4-dibromophenyl)aminium hexachloroantimonate.

On the other hand, the barrelenes (19) are not susceptible to such a rearrangement, and spectra of the parent radical cations can sometimes be observed. Thus, if the hexamethylbenzobarrelene (20) is photolyzed in dichloromethane in the presence of aluminum chloride, the ESR spectrum of the corresponding radical cation is apparent.[50]

(18)   **(19)**   **(20)**
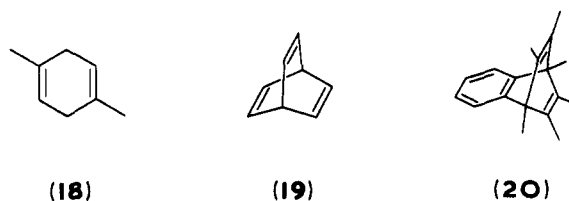
The magnitudes of the hyperfine coupling constants show that the product is essentially a cyclohexa-1,4-diene radical cation. With little delocalization of the unpaired electron into the aromatic ring and with the cyclohexadiene ring in a boat conformation, the bridgehead substituents show zero or very small coupling constants, whereas in a Freon matrix the planar cyclohexa-1,4-diene radical cation shows a hyperfine coupling with the methylene groups of 67.1 G.[47,48]

Under the same conditions, dibenzobarrelene shows only the spectrum of the anthracene radical cation; presumably the first-formed radical cation rapidly undergoes a retro-Diels–Alder reaction, the reverse of Bauld's cycloaddition (eq 20).[50] The triptycene (tri-

(20)
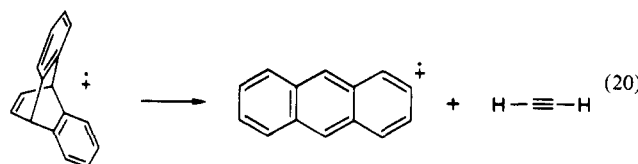
benzobarrelene) radical cation dissociates less readily, and its ESR spectrum can be observed up to about 0 °C, when it is replaced by that of the anthracene radical cation.[51]

Conclusion

The ESR spectra of the simple types of radical cations which were missing in 1980 have now been observed, but there is still a need for better methods of oxidation. The various techniques which are available are followed largely empirically, and little is known of the detailed mechanisms of the oxidations and of the relation between processes in which either one or two electrons are transferred with, for example, aluminum chloride.

Similarly, there is little understanding of the significance of the counterion, whose identity is often uncertain, and it is notable that it is very rare for hyperfine coupling to the counteranion to be observed in fluid

(47) Shida, T.; Egawa, Y.; Kobodura, H.; Kato, T. *J. Chem. Phys.* 1980, *73*, 5963.
(48) Tabata, M.; Lund, A. *Chem. Phys.* 1983, *75*, 379.
(49) Davies, A. G.; Hay-Motherwell, R. S.; Evans, J. C.; Rowlands, C. C. *J. Chem. Soc., Chem. Commun.* 1986, 1513.

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(51) Courtneidge, J. L.; Davies, A. G.; Lampard, J.; McGuchan, D. C.; unpublished work.

solution. Many of these questions could be probed by electrochemical methods, which as yet have been underexploited.

Little is known of the reaction of radical cations with other reagents, but the examples described here in which cyclobutadiene radical cations are formed from acetylenes, the biphenyl radical cation from benzene, azulene radical cations from arylacetylenes, and Diels–Alder dimers from dienes suggest that they may have a considerable potential in organic synthesis, and it may be possible to take advantage here of differences in the orbital symmetry requirements of pericyclic reactions involving RH and RH$^{\bullet+}$.

Models for Phase Equilibria in Fluid Mixtures†

Robert L. Scott

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

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Introduction

First, I want to express my appreciation for the unexpected honor of receiving the 1984 Hildebrand Award. Any American Chemical Society award is a great honor, but for me with my long association with Joel Hildebrand this one is especially pleasing and appropriate.

My own interest in phase equilibria started with my Princeton Ph.D. research on high polymer solutions.[1] Unlike most scientists, I progressed (or retrogressed) from polymers to simpler and simpler systems, like mixtures of methane and krypton.[2]

My long association with Joel Hildebrand started in 1946, when I started what became 2 years of a postdoctoral appointment; that association covered nearly all of my scientific life, but only a small fraction of his! Working with him on the third edition of *Solubility of Nonelectrolytes* whetted my interest in phase diagrams.

Hildebrand used his "regular solution" model to interpret the behavior of solutions and, in particular, to explain solubility of nonelectrolytes,[3–7] an important example of phase equilibrium. This model combines the assumption of an ideal entropy of mixing at constant volume with a kind of volume-fraction random-mixing formulation of the constant-volume energy of mixing, resulting in a simple equation for the molar Gibbs free energy of mixing ΔG_m^M of a binary mixture

$$\Delta G_m^M = -T\Delta S_{m,ideal} + \Delta E_{m,constant\ volume,random}$$
$$= RT(x_1 \ln x_1 + x_2 \ln x_2) + V_m^\circ K\phi_1\phi_2 \quad (1)$$

where x_1 and x_2 are the mole fractions of the two components in the mixture and ϕ_1 and ϕ_2 are the corresponding volume fractions, defined as $x_1V_1^\circ/V_m^\circ$ and $x_2V_2^\circ/V_m^\circ$, respectively. V_1° and V_2° are the molar volumes of the two pure liquids, and $V_m^\circ = x_1V_1^\circ + x_2V_2^\circ$. The factor K is a constant, essentially the energy (per unit volume) of making 1–2 pair interactions by breaking 1–1 and 2–2 pair interactions. If the unlike (1–2) interaction energy can be written as the geometric mean of the like (1–1 and 2–2) interaction energies, a further simplification results:

$$K = (\delta_1 - \delta_2)^2; \qquad \delta_i = (\Delta E_i^\circ/V_i^\circ)^{1/2} \quad (2)$$

Here the δ_i's are the Hildebrand "solubility parameters", calculated as the square roots of the energies of vaporization per unit volume of the pure liquids.

It has long been recognized that eq 1 is not entirely self-consistent. In order to produce a nonzero energy of mixing, there have to be differences in the energies of interaction of 1–1, 1–2, and 2–2 nearest-neighbor pairs; if so, the probabilities of finding the different pairs will not be exactly random, and the entropy of mixing cannot be exactly ideal. The corrections necessary to make eq 1 self-consistent are frequently relatively small and are therefore often neglected. The simple eq 1, even with the further simplification of eq 2, fits approximately a wide variety of nonpolar nonelectrolyte mixtures.

The earliest substantial attempts to account for equilibrium between phases came from van der Waals and other members of the Dutch school of chemical

Robert L. Scott was born in Santa Rosa, CA, in 1922. He received his S.B. from Harvard in 1942 and his Ph.D. in physical chemistry from Princeton in 1945 for research with Michel Magat and Hugh S. Taylor. After 2 years of postdoctoral work with Joel H. Hildebrand at the University of California, Berkeley, he joined the faculty at the University of California, Los Angeles, where he is now professor of physical chemistry. His research has included studies on high polymer solutions, charge-transfer complexes, enthalpies of mixing and volume changes in nonelectrolyte solutions, fluorocarbon mixtures, solubilities and phase equilibria, and critical and tricritical phenomena. He received the 1984 ACS Joel Henry Hildebrand Award in the Theoretical and Experimental Chemistry of Liquids for "seminal theoretical and experimental investigations that have related thermodynamic properties of solutions to intermolecular forces and have explained and correlated complex phase behavior in fluid mixtures".

† Adapted from the Hildebrand Award Address, American Chemical Society Meeting, St. Louis, April 9, 1984.

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