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STRUCTURES AND REACTIONS OF RADICAL CATIONS OF SOME BICYCLOALKANES AND THEIR RELATED ALKENES AS STUDIED BY 4 K MATRIX ESR

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Abstract—The σ radical cations of most typical bicycloalkanes such as norbornane and bicyclo[2,2,2]octane are radiolytically produced at 4 K in halogenocarbon matrices and are studied by ESR spectroscopy. Their electronic and geometrical structures as well as their dynamical behaviors have been elucidated from the hyperfine structures and their temperature changes. The semi occupied molecular orbital (SOMO) of the former cation is $4a_2$, in which the unpaired electron delocalizes over the four *exo* C—H bonds giving large hyperfine coupling. The latter is a Jahn–Teller active species and exhibits static distortion from D_{3h} to C_{2v} at 4 K in $\mathrm{CFCl_3}$, and the SOMO is likely to be $6b_2$, in which the unpaired electron delocalizes over the four *endo* C—H bonds giving large proton coupling, although a dynamically averaged structure with 12 equivalent methylene protons is observed in c-$\mathrm{C_6F_{12}}$ as well as in $\mathrm{CFCl_2CF_2Cl}$ matrices at 77 K. The unpaired electron distribution in bicycloalkane radical cations is similar to that in cycloalkane radical cations previously studied. Upon warming both the cations undergo deprotonation to give 2-yl alkyl radicals from the *exo* or *endo* C—H bond, at which the higher unpaired electron density is populated. In addition to these radical cations, the structures and reactions of the radical cations of the related bicycloalkenes such as norbornadiene, quadricyclane, and bicyclo[2,2,2]octene have also been studied. The hydride ion transfer to an olefinic radical cation to form an alkyl radical is observed for the bicyclo[2,2,2]octene radical cation as the first example observed by ESR.

INTRODUCTION

During the past half decade we have concentrated our efforts to systematic studies of structures and reactions of σ radical cations of prototype alkanes including linear,[1-4] branched[1,3-6] and cycloalkanes.[7,8] In a continuation of our studies, radical cations of typical bicycloalkanes such as bicyclo[2,2,1]heptane (norbornane) and bicyclo[2,2,2]octane have been studied together with some related compounds such as 2,5-norbornadiene, quadricyclane, and bicyclo[2,2,2]oct-2-ene. Among these, the preliminary results of ESR spectra and structures of norbornane and norbornadiene have already been reported.[9] In the present work, the reactions of these species will be described together with the spectra, structures, and reactions of other related species mentioned above.

Our main interest in alkane radical cations is in their unpaired electron in the σ bonding orbital, especially in the delocalization of the unpaired electron in the σ molecular frame.[1-9] Since σ radical cations of alkanes were not studied by ESR until recently, information on the σ unpaired electron orbital has been very limited. Symons and Smith have suggested that the unpaired electron in $\mathrm{Me_3C\overset{\dot{+}}{-}CMe_3}$($\mathrm{HME^+}$) is confined to the central C—C bond and couples with six protons having perhaps an eclipsed (or staggered) conformation with respect to the unpaired electron orbital.[10] As a similar example, Alder *et al.*[11] have further studied [3,3,3]propellane, in which the unpaired electron is confined to the central C—C bond combining the two bridgehead carbon atoms.

On the other hand, we have shown that the unpaired electron is delocalized along the C—C zig-zag chain in the linear alkane radical cations with a fully extended structure ($\mathrm{C_2H_6^{\dot{+}}}$–n-$\mathrm{C_{14}H_{30}^{\dot{+}}}$).[1,2] As a result, the two in-plane end C—H bonds participate in the σ molecular orbital giving a proton hyperfine coupling as large as, for example, 150 G in $\mathrm{CH_3CH_3^{\dot{+}}}$ and 98 G in $\mathrm{CH_3CH_2CH_3^{\dot{+}}}$. The out-of-plane proton couplings are less than 10 G since they are located in the nodal plane of the unpaired electron orbital.[1-3] We have further shown that the cycloalkane radical cations (c-$\mathrm{C_3H_6^{\dot{+}}}$–c-$\mathrm{C_8H_{16}^{\dot{+}}}$) are also characterized as σ-delocalized radicals, in which the unpaired electron is delocalized over the molecular orbital in the equatorial plane and thus the equatorial C–H bonds participate in the unpaired electron orbital giving a large proton hyperfine coupling (e.g. 85 G in c-$\mathrm{C_6H_{12}^{\dot{+}}}$) like the in-plane end C—H protons in the linear alkane cations.

In contrast, the unpaired electron in the radical cations of highly branched alkanes such as $\mathrm{Me_3CH}$, $\mathrm{Me_4C}$ and a variety of methyl substituted n-butanes is more confined to a particular C—C bond so as to maximize the hyperconjugative effect.[5] The results are in line with the interpretation of $\mathrm{HME^+}$ by Symons and Smith.[10] Wang and Williams have confirmed Symons and Smith's assignment of the spectrum to $\mathrm{HME^+}$[12] and have extended their studies to n-butane and n-hexane radical cations[13] following our study.[1,2] They have explained the spin delocalization in $\mathrm{HME^+}$ in terms of a W-plan model[11] and have extended this explanation to the n-butane radical cation.[13] On the other hand, we have suggested that linear alkane radical cations are not in line with the branched alkane radical cation such as $\mathrm{HME^+}$ as is mentioned above.[3,5]

Now, in our preliminary work on the norbornane radical cation we have shown that the four *exo* C—H bonds participate in the $4a_2$ unpaired electron orbital giving an *exo* proton coupling as large as 65 G.[9] This is in line with the in-plane end protons in the linear alkane radical cations[1-3] as well as with the equatorial protons in cycloalkane radical cations.[7,8] In this work, to characterize the σ delocalization in the bicycloalkane radical cations, studies are further extended to the bicyclo[2.2.2]octane radical cation, which is of particular interest as a Jahn-Teller active species.

In addition to such structural interest, the reactions of one electron loss species from the σ-bonding orbital of alkanes are of fundamental importance. We have shown that radical cations of alkanes thermally convert into alkyl radicals by deprotonation from the C—H bond in which the unpaired electron is highly populated.[1,3,6] In this respect, the relation between the unpaired electron distribution and the reaction site of bicycloalkane radical cations are of considerable interest.

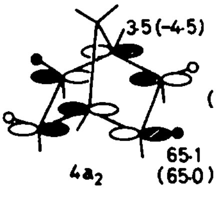
The related radical cations produced from norbonadiene and quadricyclane may be of particular interest because the photochemical conversion of their parent molecules have drawn considerable interest in the field of photochemical storage of solar energy. In this paper, the structures and reactions of these radical cations are also studied together with those of some related bicycloalkene radical cations.

RESULTS

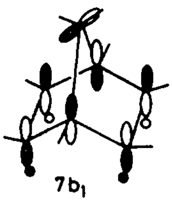
Bicyclo[2,2,1]*heptane* (*norbornane*)

As is briefly described in our preliminary communication,[9] the radical cation of norbornane radiolytically produced at 4 K in $CFCl_2CF_2Cl$ exhibits an equally spaced five-line spectrum with a binomial intensity ratio and a splitting of 65.1 G (4H), which can be ascribable to a coupling with the four equivalent *exo* or *endo* protons (Fig. 1(a)). In the present work, the five-line spectrum is found to be further split into 1 : 2 : 1 three-line substructures with a 3.5 G (2H) coupling at 100 K as shown in Fig. 1(b). The two equivalent protons responsible for the three-line substructures are the two tertiary protons at the bridgehead carbons or the methylene protons at C_7.

Now, in referring to the *ab initio* calculation of the parent molecule,[14] the candidates for the unpaired electron orbital are the highest two orbitals, $4a_2$ and $7b_1$, in which the *exo* and *endo* C—H bonds, respectively, participate in the delocalized σ molecular orbital as shown below.



(I)



(II)

As is seen in I, the methylene protons at C_7 cannot take part in the $4a_2$ SOMO because hyperconjugation to these protons are symmetry forbidden so that the 3.5 G (2H) coupling must arise from the two tertiary protons. Because of the unpaired electron densities at the bridgehead carbon atoms, a small α-proton coupling with the negative sign is expected for these protons. On the other hand, if the $7b_1$ SOMO is the case, both the methylene and tertiary protons may give a small α-coupling with a similar magnitude, resulting in a five-line substructure. So, the three-line substructure is more preferential to the $4a_2$ SOMO.

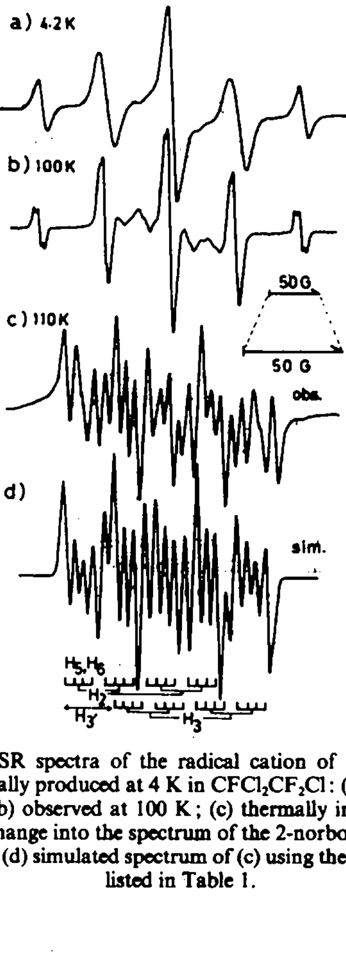
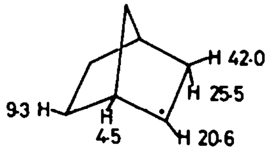


Fig. 1. ESR spectra of the radical cation of norbornane radiolytically produced at 4 K in $CFCl_2CF_2Cl$: (a) observed at 4 K; (b) observed at 100 K; (c) thermally induced irreversible change into the spectrum of the 2-norbornyl radical at 110 K; (d) simulated spectrum of (c) using the parameters listed in Table 1.

In order to confirm this expectation, the trial INDO calculations have been performed assuming the molecular geometry of the parent norbornane determined by electron diffraction.[15] The results indicate that the $4a_2$ orbital is indeed the SOMO, in which the *exo* and tertiary proton couplings are 65.0 and −4.5 G, respectively, in excellent agreement with the observed coupling constants as shown in parentheses in I and in Table 1. The couplings to the rest of the protons ($\leqslant 0.3$ G) are too small to be resolved and may be hidden in the linewidth as is observed. Furthermore, the coefficients of the $7b_1$ orbital show that the *endo* proton coupling is smaller by a factor of 0.7 than the *exo* proton coupling in the $4a_2$ orbital. In addition, both the C_7 and the bridgehead carbon atoms participate in the $7b_1$ orbital with similar contributions supporting our expectation mentioned above. The *ab initio* calculations of the parent molecule[14] also show a similar trend with our trial INDO calculations. From these results, it is concluded that the radical cation of norbornane possesses the $4a_2$ SOMO, in which the $C—H_{exo}$ bonds participate to give a very large *exo* proton coupling (65.1 G).

Now, upon further warming to 110 K, the irreversible spectral change into a complex spectrum (Fig. 1(c)) was observed. The hyperfine multiplet can be interpreted by the proton couplings of 42 (1H), 25.5 (1H), 20.6 (1H), 9 (1H), and 4.5 G (1H) as shown by the stick diagram under the spectrum in Fig. 1(d). The simulated spectrum (Fig. 1(d)) using these coupling constants shows excellent agreement with the observed spectrum. The coupling constants are in agreement with those reported for the 2-norbornyl radical, which is produced by the breakage of the C—H_{exo} bond.[16]

The protons responsible for these couplings are shown in III. For simplicity, the C—H bonds which do not exhibit resolvable couplings are omitted.



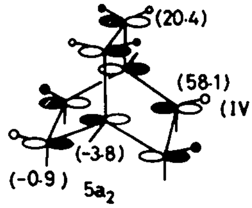
(III)

The inequivalent β-proton couplings of 42 and 25.5 G as well as the relatively small α-proton coupling of 20.6 G suggest that the radical carbon atom possesses a slightly bent structure preserving the configuration of the parent cation after the detachment of the *exo* proton. The deprotonation of the *exo* proton from the radical cation of norbornane with the $4a_2$ SOMO to form the 2-norbornyl radical is quite reasonable supporting our interpretation of the spectrum.

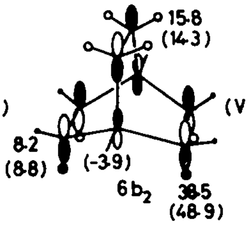
Bicyclo[2,2,2]*octane*

Shown in Fig. 2(a) is the spectrum observed at 4 K in $CFCl_3$ after irradiation at the same temperature. The spectrum is very complicated even upon warming above 77 K, because of incomplete dynamic average in this matrix. On the other hand, an equally spaced thirteen-line spectrum with a binomial intensity ratio and with a splitting of 20 G (12H) is observed in perfluorocyclohexane (c-C_6F_{12}) at 77 K as shown in Fig. 2(c), although the almost structureless broad spectrum was observed at 4 K because of motional broadening. The 12 equivalent coupling protons at 77 K are unequivocally ascribable to the protons in six methylene groups. The coupling to the tertiary protons at the bridgehead carbon atoms may be too small to be resolved. The resolution of the hyperfine multiplet at 4 K is best in $CFCl_3$ (Fig. 2(a)). It indicates that the 12 coupling protons are not equivalent at 4 K suggesting a distortion of the symmetrical structure with C_3 symmetry.

Now, *ab initio* studies[14] suggest that the highest occupied orbital of the parent molecule with D_{3h} symmetry is the double degenerate e_g orbital. So, it is expected that loss of an electron leads to Jahn–Teller instability. A C_{2v} distortion by the Jahn–Teller active CCC bending mode results in the splitting of the e_g orbital into the a_2 and b_2 orbitals shown in IV and V.



(IV)



(V)

Although the electron diffraction study[15] shows that the CH_2—CH_2 group slightly twists around the C—C bond reducing the D_{3h} symmetry of the parent molecule into C_{3v}, the C_{2v} distortion may lead to similar

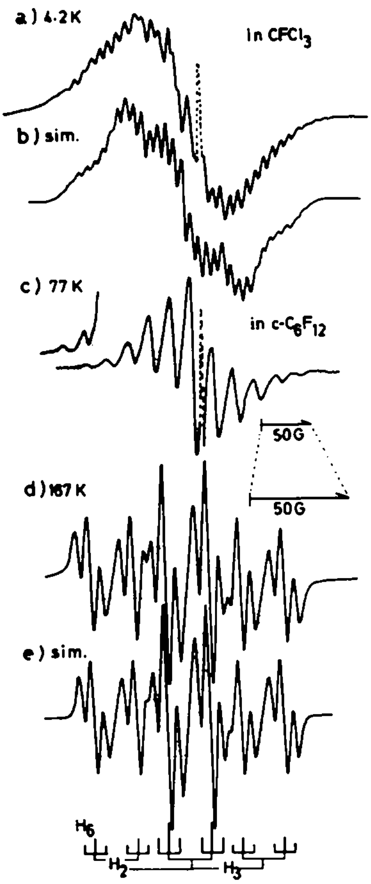


Fig. 2. ESR spectra of the radical cation of bicyclo[2,2,2]octane radiolytically produced at 4 K: (a) observed at 4 K in $CFCl_3$; (b) simulated spectrum of (a) using the parameters listed in Table 1; (c) observed at 77 K in c-C_6F_{12}; (d) thermally induced irreversible change of (c) into the spectrum of the bicyclo[2,2,2]oct-2-yl radical at 167 K; (e) simulated spectrum of (c) with the parameters listed in Table 1. The dotted lines in (a) and (c) are due to the colored center of the sample tube.

Jahn–Teller split levels as shown above. In the a_2 and b_2 orbitals the 12 protons, except the tertiary ones, consist of the three sets of four equivalent protons, namely, *exo*, *endo*, and the —CH_2CH_2— bridge protons. The spectrum observed at 4 K in $CFCl_3$ can be simulated based on the three sets of coupling constants, 38.5 (4H), 15.8 (4H), and 8.2 G (4H) as shown in Fig. 2(b). These coupling constants may be ascribable to the *exo*, bridge, and *endo* protons, respectively, if the a_2 orbital is the case, whereas the *endo*, bridge, and *exo* protons, respectively, if the b_2 orbital is the case. Since the coupling to the tertiary protons in the radical cation of norbornane is as small as 3.5 G, they are supposed to be hidden in the linewidth in this case.

In order to discriminate between the a_2 and b_2 orbitals, trial INDO calculations have been performed. When the dihedral angle of the two CCCC planes is decreased to 105° by the distortion along the Jahn–Teller active degenerate CCC bending mode, the total energy is minimized with the lowering of the b_2 orbital by the increasing bonding nature in the basal C—C bonds resulting in the a_2 SOMO with the coupling constants given in parentheses in IV. On the

Table 1. Geometrical and electronic structures and ESR parameters of radical cations and the secondary radicals formed by their thermal reaction

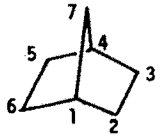
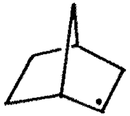
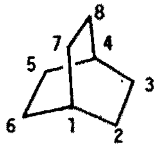
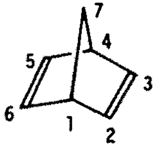
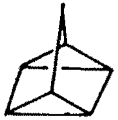
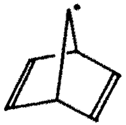
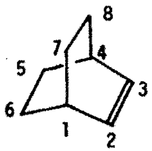
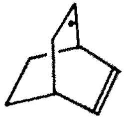
Molecules	Matrices (Temp.)	Cation Radicals				Product of Thermal Reactions				
		SOMO	h.f. couplings(Gauss)		g	Radicals	g	h.f. couplings		
			Observed	INDO Values				Observed	Literature Values	(Ref)
	$CFCl_2CF_2Cl$ (100 K)	$4a_2$	65.1(4H) 3.5(2H)	65.0(H_{exo}) -4.5(H_1)	2.0052		2.0026	42.0(1H) 25.5(1H) 20.6(1H) 9.3(1H) 4.5(1H)	41.7(H_3) 25.6($H_{3'}$) 20.6(H_2) 9.0(H_6) 5.5(H_5)	(16)
	$CFCl_3$	$6b_2$	38.5(4H) 15.8(4H) 8.2(4H)	[$6b_2$] 48.9(H_{end}) 14.3($H_{7,8}$) 8.8(H_{exo}) -3.8($H_{1,4}$)	2.0098[a]		2.0033	36.8(2H) 21.5(1H) 5.5(2H)	37.0($H_{3,3'}$) 21.5(H_2) 5.7(H_6)	(17)
	$c\text{-}C_6F_{12}$ (77K)		20.0(12H)	[$5a_2$] 58.1(H_{exo}) 20.4($H_{7,8}$) -0.9(H_{end}) -3.9($H_{1,4}$)	2.0059					

Table 1.—*Continued.*

 	$CFCl_2CF_2Cl$ (100K)	$6b_2$	8.2(4H) 3.3(2H)	-5.8(H) 2.1(H_7)	2.0024		2.0028	18.5(1H)	4.5(H_7)	(19)
	$CFCl_2CF_2Cl$ (4.2K)	$5b_2$	20.4(2H)	-10.5($H_{2,3}$) -1.3(H_{exo}) 0.2(H_{end})	2.0025		2.0026	36.6(1H) 32.0(1H) 20.8(1H) 6.2(1H)	36.6(H_9) 30.9($H_{9'}$) 20.8(H_8) 6.3(H)	(21)
	(77K)		9.0(4H)					41.0(1H) 36.0(1H) 18.0(1H) 5.6(1H)		

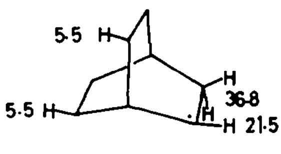
^{a}The crossover point of the first-derivative spectrum.

other hand, the increase of the dihedral angle gives the energy minimum at 130° with the lowering of the a_2 orbital by the increasing bonding nature of the basal C—C bonds resulting in the b_2 SOMO with the coupling constants given in V. Although the $^2A_2$ state is lower in energy by *ca* 3 kcal mol^{-1} than the $^2B_2$ state, the observed smallest coupling of 8.2 G seems to be too large for the *endo* protons (-2 G), which lie close to the nordal plane of the unpaired electron orbital in the a_2 orbital. On the other hand, the C—H_{exo} bond is slightly out of the nodal plane of the unpaired electron orbital in the b_2 distortion so that a considerably large positive α-coupling of 8 G arises in agreement with the observed value. Although the a_2 SOMO with a lower energy cannot be completely excluded, the b_2 SOMO seems to be more preferential to account for the observed coupling constants.

The spectrum observed at 77 K in c-C_6F_{12} with the 12 equivalent protons (20.0 G) can be explained by the dynamical average (20.8 G) of the three sets of coupling constants observed at 4 K in $CFCl_3$. The dynamic Jahn–Teller effect may be responsible for this dynamic process as are other Jahn–Teller active radical cations previously studied by us.[1–8] The broad 13-line spectrum with the same coupling constant was also observed in $CFCl_2CF_2Cl$ at 77 K.

The marked characteristic of this radical cation is the large positive g-shift ($\sim$2.01), which may be expected from the Jahn–Teller split levels with a relatively small energy difference as will be discussed in a later section.

Upon warming to 167 K, the 13-line spectrum in c-C_6F_{12} irreversibly changes to the spectrum shown in Fig. 2(d). The spectrum can be simulated by the coupling constants of 36.8 (2H), 21.5 (1H), and 5.5 G (2H), which may be ascribable to the bicyclo[2,2,2]oct-2-yl radical as shown in VI.[17] Essentially the same spectrum is observed in $CFCl_2CF_2Cl$ at 115 K. The two equivalent β-H couplings of 36.8 G indicate that the radical carbon atom has a planar configuration, which is supposed to result from a dynamical average of the bent structure because of a relatively small α-H coupling of 21.5 G. In this case, it is not possible to discriminate which proton is detached from the *exo* or *endo* C—H bond, even more, which bridge proton is detached. However, the detachment of the bridge proton rather than the tertiary one is reasonable in view of the unpaired electron distribution in the b_2 or a_2 SOMO.



(VI)

2,5-*Norbornadiene and quadricyclane*

As is briefly described in our preliminary communication,[9] the radical cation of norbornadiene produced at 4 K in $CFCl_2CF_2Cl$ gives a poorly resolved spectrum at 4 K (Fig. 3(a)), which exhibits a well resolved 5 × 3 line spectrum at 100 K (Fig. 3(b)). The simulated spectrum (Fig. 3(c)) with coupling constants of 8.2 (4H) and 3.3 G (2H) is in good agreement with the observed spectrum. The coupling constant of 8.2 G (4H) is unequivocally ascribable to the four α-protons attached to the —$CH\overset{+}{=}CH$— bond in the π radical cation. The coupling constant of 3.3 G (2H) is attributable to the methylene protons at C_7 rather than the tertiary protons at the bridgehead carbons, because the former can participate in the SOMO, whereas the hyperconjugative effect is minimal for the latter with a dihedral angle of *ca* 90°. The trial INDO calculations show that an elongation of the C=C bond (1.443 Å) leads to the $6a_2$ SOMO with coupling constants of -5.8 (4H), -2.1 (2H), and -1.4 G (2H) for the basal, the C_7, and the tertiary protons, respectively. Although we have not been aware, the referee drew our attention to recent papers on the CIDNP studies of radical cations of norbornadiene and quadricyclane by Roth and co-workers.[18a,b] Their *ab initio* calculation gives the coupling constants -13.0 (4H), 2.8 (2H), and -0.7 G (2H), respectively, for these protons. The observed basal proton coupling is in between the two calculated values.

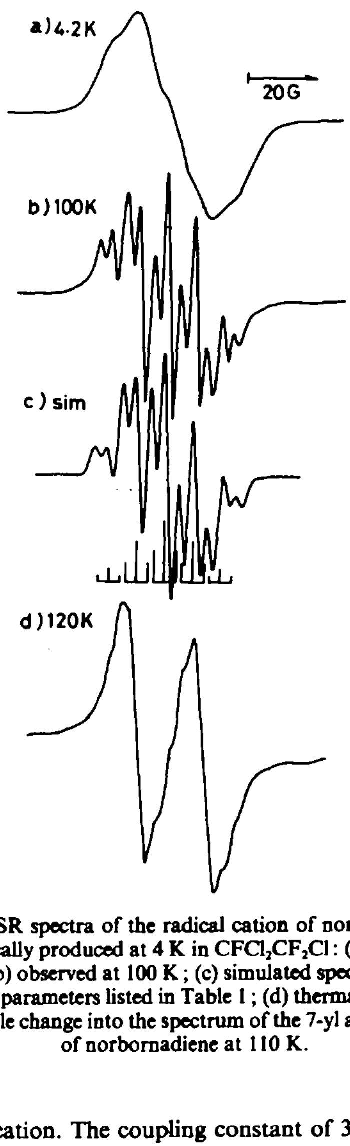
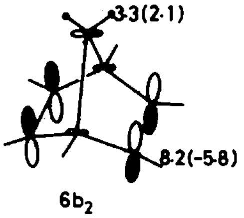


Fig. 3. ESR spectra of the radical cation of norbornadiene radiolytically produced at 4 K in $CFCl_2CF_2Cl$: (a) observed at 4 K; (b) observed at 100 K; (c) simulated spectrum of (b) using the parameters listed in Table 1; (d) thermally induced irreversible change into the spectrum of the 7-yl alkyl radical of norbornadiene at 110 K.

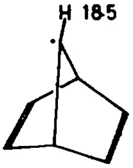
In the present work, it has been further found that quadricyclane in $CF_2ClCFCl_2$ exhibits essentially the same spectrum as that obtained from norbornadiene even at 4 K. A parallel result is obtained from the optical study.[18c] Since the CIDNP studies show that the radical cations of quadricyclane and norbornadiene are discrete species,[18a,b] it is likely that the



(VII)

radical cation of quadricyclane isomerizes into that of norbornadiene during irradiation at 4 K. The radical cation of norbornadiene is extremely sensitive to visible light and exhibits an interesting spectral change. The details will be given in a separate paper together with some photoinduced changes of other radical cations.

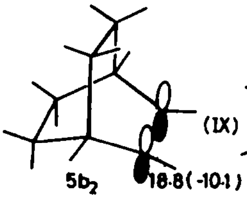
Upon warming to 110 K in the dark the spectrum of the radical cation of norbornadiene changes into the two-line spectrum (Fig. 3(d)) with a coupling constant of 18.5 G (1H), which is attributable to the 7-yl alkyl radical (VIII) formed from deprotonation of the radical cation at C_7 rather than at the bridgehead carbons. The deprotonation of the C_7 proton is reasonable because of the unpaired electron densities in the C–H bonds at C_7 as shown in VII. The 7-yl alkyl radical of norbornadiene derived from the bromide by photolysis exhibits extremely small α-proton coupling (4.5 G), which is attributed to the strongly bent structure at the radical carbon atom.[16b,19] However, our radical derived from the radical cation exhibits a normal value for the slightly bent radical carbon.



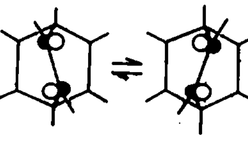
(VIII)

Bicyclo[2,2,2]*oct-2-ene*

As shown in Fig. 4(a), the radical cation of bicyclo[2,2,2]octene produced at 4 K in $CFCl_2CF_2Cl$ gives a simple 1 : 2 : 1 three-line spectrum with a coupling constant of 20.4 G (2H), which is attributable to the two α-protons attached to the —CH$\overset{+}{=}$CH— bond (IX). A relatively large olefinic α-coupling might be due to twisting around the —CH$\overset{+}{=}$CH— bond (X).[20] The tertiary proton couplings are supposed to be too small to be resolved. However, upon warming to 106 K the three-line spectrum exhibits a reversible change into a five-line spectrum with a coupling constant of about 9 G as shown in Figs 4(b) and (c). The temperature change may be ascribable to the ring puckering motion of the twist —CH$\overset{+}{=}$CH— bridge (X), which is expected to reduce the vinylene proton coupling because of the sign alternation at the planar structure and to increase the bridgehead tertiary proton coupling because of the increasing averaged $\langle\cos^2\theta\rangle$, where θ is the dihedral angle of the bridgehead tertiary C—H bond with respect to the unpaired electron orbital.



(IX)



(X)

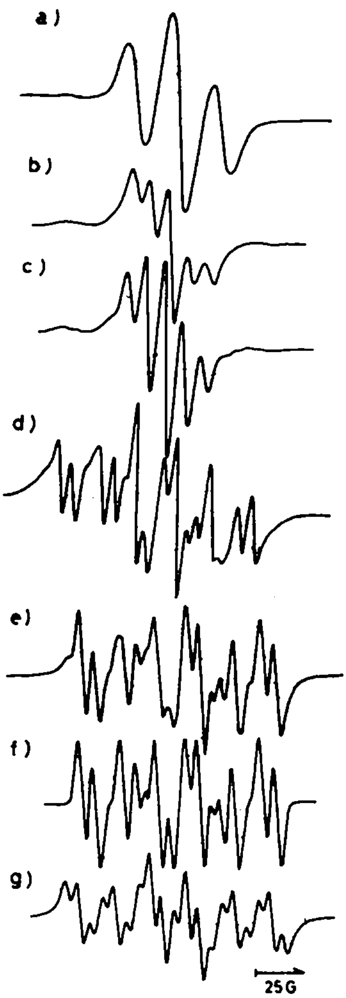
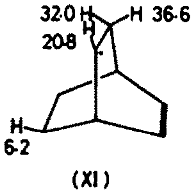
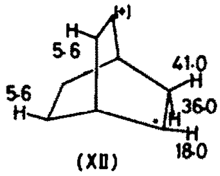


Fig. 4. ESR spectra of the radical cation of bicyclo[2,2,2]octene radiolytically produced at 4 K in $CFCl_2CF_2Cl$: (a) observed at 4 K; (b) observed at 101 K; (c) observed at 104 K; (d) thermally induced irreversible change into the spectrum of bicyclo[2,2,2]oct-7-yl and -2-yl radicals at 110 K; (e) simulated spectra of (d) as the 1 : 1.5 superposition of (f) and (g); (f) and (g) the simulated component spectra of bicyclo[2,2,2]oct-7-yl and -2-yl radicals, respectively, using the parameters listed in Table 1.

Upon further warming to 110 K, the irreversible spectral change occurs as shown in Fig. 4(d). The most plausible species is the bicyclo[2,2,2]oct-7-yl radical (XI),[21] which is formed from deprotonation at C_7. However, the spectrum exhibits extra lines, which cannot be accounted for by the single species as shown in Fig. 4(f). The extra lines are likely ascribable to the bicyclo[2,2,2]oct-2-yl radical (XII), which is formed from the inter- or intramolecular hydride ion (H^-) transfer to the olefinic bond (Fig. 4(g)). The observed spectrum is fairly well reproduced by the 1 : 1.5 superposition of the two spectra as shown in Fig. 4(e). To the best of the authors knowledge, the latter reaction provides the first example of the H^- transfer in the olefinic π radical cation detected by ESR.[22]



(XI)



(XII)

DISCUSSION

Structures and reactions of radical cations of bicycloalkanes

The unpaired electron distributions in the radical cations of the two typical bicycloalkanes have been studied. The results indicate that the unpaired electron delocalizes over the σ molecular frame as is the case of radical cations of linear and cycloalkanes previously studied by us. The *exo* or *endo* C—H bonds participate in the σ molecular orbital depending upon the symmetry of the orbital. As a result, they exhibit a large proton coupling characteristic of σ radical cations. This is in marked contrast to the olefinic π radical cations formed from the related bicycloalkenes. The situation is similar to the two in-plane C—H bonds in the $2b_2$ orbital of the radical cation of propane[1-4] as well as the equatorial C—H bonds in the radical cations of cycloalkanes from c-C_4 to c-C_8.[7,8]

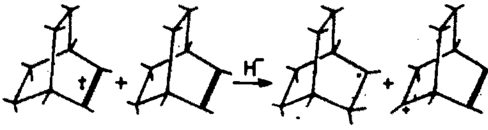
In our previous studies on radical cations of linear and branched alkanes, we have shown that the alkane radical cations undergo bimolecular deprotonation from the C—H bond, in which the unpaired electron is highly populated.[1-4,6] In the case of cycloalkanes,[7] however, it was not possible to obtain evidence for such a position selectivity in deprotonation because all of the protons involved are from the methylene group and the structures of the resulting alkyl radical is not informative. On the other hand, bicycloalkanes provide us with a good example to discriminate the position selectivity of deprotonation. The results obtained in the present work give further confirmation to the previous conclusion derived from linear and branched alkane radical cations.

It has been further found that the radical cations of related bicycloalkenes also deprotonate from the expected C—H bond to form alkyl radicals as is summarized in Table 1 together with the results obtained from bicycloalkanes.

It is to be noted that the deprotonation of alkane radical cations to form alkyl radicals is dependent upon the matrix and is exclusively observed in $CFCl_2CF_2Cl$ and in SF_6 but is not in $CFCl_3$ in our previous work.[1-9] In the present work, the radical cation of bicyclo[2,2,2]octane in c-C_6F_{12} also undergoes deprotonation as in $CFCl_2CF_2Cl$.

Hydride ion transfer to olefinic radical cations to form alkyl radical

In addition to deprotonation to form alkyl radicals, the olefinic π radical cation of bicyclo[2,2,2]octene in $CFCl_2CF_2Cl$ has been found to undergo hydride ion transfer reaction to the olefinic $—CH\overset{+}{\cdot\cdot}CH—$ bond to form 2-yl alkyl radical. This gives the first ESR evidence for this type of reaction, which is a well-known ion-molecule reaction in the gas phase for olefinic radical cations with alkanes to give alkyl radicals,[22] although there is a possibility of intramolecular H^- transfer in our case. The occurrence of the two types of reactions, that is, deprotonation and H^- transfer, may be due to the dual nature of alkane and alkene radical cations.



(XIII)

Jahn–Teller distortion of the radical cation of bicyclo[2,2,2]octane

Static and dynamic Jahn–Teller effects have been observed in one of the most typical bicyclic radical cations. Since it is hard to believe that molecular reorientation around the C_3 axis to average out the interaction with the surrounding matrix field, which might well be the cause of the distortion, takes place at 77 K, the example studied in the present work may provide further evidence for the Jahn–Teller distortion which may be caused mainly by the intramolecular interactions. Nevertheless, the activation energy of the dynamical averaging process is seriously affected by the kind of matrices as is the case of other Jahn–Teller active radical cations previously studied by us.[1-3,7,8] This may suggest that the Jahn–Teller potential surface in the trough is sensitive to the environment and that the distorted structure determined by the intramolecular interactions is further stabilized by the interaction with the matrix as is discussed in our previous paper.[8] At any rate, it is quite meaningful that Jahn–Teller active radical cations of alkanes are almost exclusively accompanied by the dynamic process, which averages hyperfine couplings at relatively low temperature, although the other cations do not always exhibit such dynamical behaviors at low temperature.

g-Shift in the radical cation of bicyclo[2,2,2]octane

As is pointed out in our previous paper,[8] Jahn–Teller active σ radical cations potentially possess a possibility to exhibit a large positive g-shift, because the Jahn–Teller split σ levels have electron configurations of $\ldots(\sigma_x)^2(\sigma_y)^1$ and $\ldots(\sigma_x)^1(\sigma_y)^2$, which can be mixed by the spin–orbit coupling. Such a mixing cannot be expected in the Jahn–Teller split levels in aromatic radical ions, because the electron configuration of $\ldots(\pi)^2(\pi')^1$ and $\ldots(\pi)^1(\pi')^2$ cannot be mixed by the spin–orbit coupling. The extremely large positive g-shift observed in the radical cation of bicyclo[2,2,2]octane (2.01) may provide us with a good example for this expectation to σ radical cations. This may be compatible with large g-values of 2.0066 and 2.0068 observed for the radical cations of cyclohexane and cyclooctane, respectively.[8]

EXPERIMENTAL

The samples of norbornane were obtained from Eastman Kodak Co., those of norbornadiene, and $CFCl_3$ from Tokyo Kasei Kogyo Co., and c-C_6F_{12} from PCR Research Chemical Inc. The samples of quadricyclane, $CF_2ClCFCl_2$, and bicyclo[2,2,2]octene were generous gifts from Dr K. Hayakawa and Dr A. Ueda of this institute, and Dr T. Kawamura of Kyoto University, respectively. The sample of bicyclo[2,2,2]octane was prepared from bicyclo[2,2,2]octene by the method described in the literature.[23] The frozen samples were prepared using a grease and mercury free vacuum line. The radical cations were radiolytically produced from solutes (0.1–0.5 mol%) in fluorchlorocarbons[2,24] and perfluorocarbons.[2,25]

The experimental setups for irradiation and successive ESR measurements at liquid helium temperature were essentially the same as those used in our previous paper.[1–9] Most of the samples were irradiated at 4 K by X-rays and some of them at 77 K by ^{60}Co γ-rays. The ESR spectra were measured by a Bruker ER-200D and a Varian E-12 spectrometer with a homemade liquid helium cryostat.

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