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ON THE CONFORMATION OF β-HALOALKYL RADICALS

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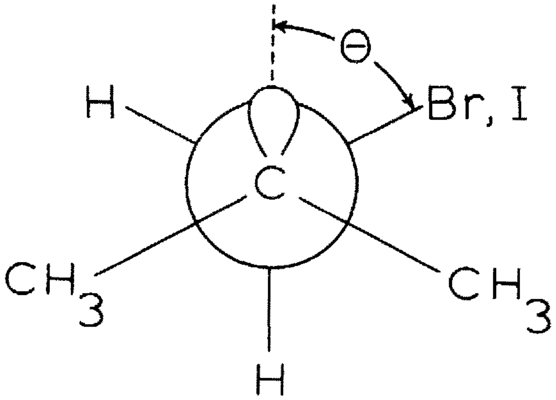
We have previously reported that the β-bromo-tert-butyl radical (I) is produced by the x-irradiation of isobutyl bromide in an adamantane matrix.[1] In view of a recent claim by Nelson and Symons[2] that the same spectrum could also be obtained by the irradiation of tert-butyl bromide in adamantane, thereby suggesting that our identification of I was incorrect, we felt it necessary to investigate the epr spectrum of x-irradiated tert-butyl bromide in adamantane ourselves.

A sample of redistilled tert-butyl bromide in adamantane prepared as previously described[1] was x-irradiated for 30 minutes at 77° K and its epr spectrum was studied as a function of temperature. The major part of the epr signal resulted from the tert-butyl radical, which would be expected since tert-butyl chloride is known to be a good source of tert-butyl radical under the same conditions.[3] A minor part of the epr signal resulted from an unknown species (II). The epr signal of I prepared from isobutyl bromide in adamantane is, however, not similar to that of II. In order to improve the resolution of the epr spectra, the tert-butyl bromide sample was also prepared in adamantane-d_{16}. At the bottom of the figure below is the second derivative epr spectrum of this sample taken at 202° K. Between the ten equally spaced lines of tert-butyl radical can be seen lines belonging to the spectrum of II, with the most intense lines ∿1/20 of those of the tert-butyl radical. At the top of the figure is the epr spectrum assigned to radical I from a similarly prepared sample containing isobutyl bromide. It is clear that the two epr spectra have nothing in common except some accidental overlap (the difference in g value is responsible for the offset). Furthermore the thermal behavior of I and II are different. I is stable below 209° K (the phase transition temperature of adamantane) but disappears almost instantly above this temperature. II begins to decay at temperatures as low as 190° K but can still be detected as high as 213° K. Thus we cannot confirm the results reported by Nelson and Symons.[2] It is possible that their results were due to isobutyl bromide present as an impurity in their sample of tert-butyl bromide.

Their alternative interpretation of our original data, namely that I is a tert-butyl radical·bromide ion complex ($Me_3C...Br^-$), seems unreasonable to us on several grounds. First, it offers no explanation for our observation that above 209° K the spectrum of I changes quantitatively to that of the monodeutero _tert_-butyl radical,instead one would expect the postulated complex to simply dissociate to ordinary _tert_-butyl radical. Second, our observed Br hfs of 6.7 is _not_ similar to the ~50 G Br hfs reported for the $CH_3...Br^-$ complex.[4] Third, the epr spectrum of I is simulated nicely by a 1:2:1 of septets of bromine quartets with the "2" intensity lines broadened by linewidth alternation.[1] The postulated halide complex would not exhibit these broad lines. Fourth, adding Me_3NBH_3 to the adamantane-_tert_-butyl bromide mixture before x-irradiation did not change the resulting epr spectrum. We have found that this technique is an effective method for producing anion radicals in the case of benzene and hexafluorobenzene,[5] penta-, tetra-, and difluorobenzene,[6] and pyridine and its fluorinated derivatives.[7]

Since the original report on the β-bromo-_tert_-butyl radical[1] we have prepared the remainder of the β-halo-_tert_-butyl radicals by x-irradiation of the isobutyl halides in an adamantane matrix.[8] We find that the fluoro radical has a large fluorine hfs with a large negative temperature dependence and that the β-protons are equivalent and small with a large positive temperature dependence (Table). Thus it apparently prefers an eclipsed goemetry similar to that of the corresponding chloro radical, but with a greater degree of rotational freedom. The iodo radical has a small iodine hfs and large inequivalent β-proton hfs similar to those of radical I. The absence of linewidth alternation in the case of the iodo radical indicates that it is more limited in rotational freedom than is I. Utilizing the usual $A + B \cos^2 \Theta$ relationship ($A = 0$) for the β-proton hfs we find that the carbon-halogen bond would make a 75° dihedral angle with the direction of the p orbital for the bromo and iodo radicals. Thus the halogens would be within 15° of eclipsed with the methyl groups for planar radicals. Because this would create a rather large steric repulsion we believe that the radicals centers must be non-planar as shown below.[9]



The value estimated for θ is 80° based on an INDO calculation for the β-proton hfs for a tetrahedral ethyl radical. This non-planarity, coupled with the high rotational barrier of the CH_2X group (3 kcal/mole minimum for radical I and greater for the iodo radical) can then explain the retention of stereochemical configuration observed for radicals of this type without having to invoke a "bridged" species.[10]

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EPR Parameters of β-halo-*tert*-butyl Radicals in Adamantane

X	F	^{35}Cl	^{81}Br	I
Temp, °K	214	215	202	208
a_x, G	103.7	19.5	6.7	7.0
a_H (CH_2)	10.4	6.3	21.4, 42.7	21.9, 43.8
a_H (CH_3)	23.3	21.1	21.4	21.9
g	2.0030	2.0042	2.0010	2.0009

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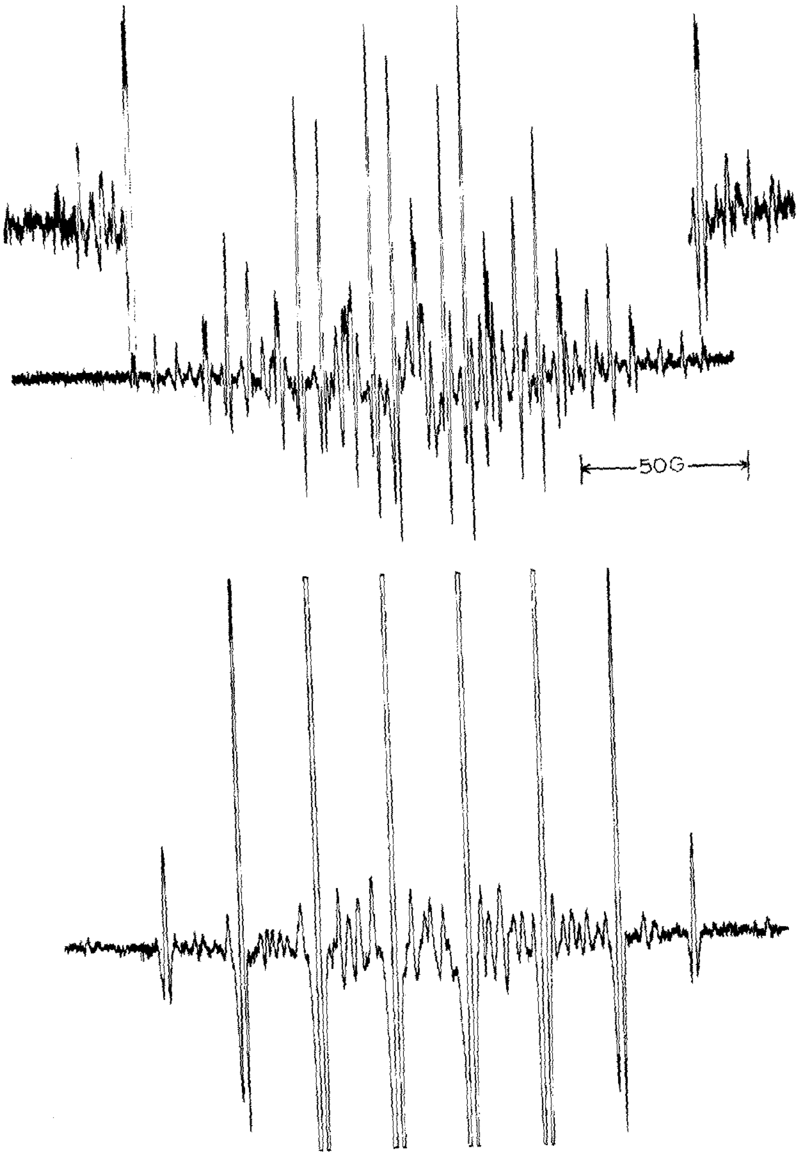

Second derivative epr spectra at 202°K of isobutyl bromide (top) and *tert*-butyl bromide (bottom) x-irradiated in an adamantane-d_{16} matrix at 77°K.