Generation and IR spectroscopic study of benzyl radical*

E. G. Baskir, A. K. Maltsev,[†] V. A. Korolev, V. N. Khabashesku, and O. M. Nefedov^{*}

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328

The benzyl radical $C_6H_5CH_2$ has been obtained by gas phase pyrolysis of two different precursors, benzyl bromide and dibenzyl, and studied in an argon matrix at 12 K by IR spectroscopy. Similarly, the deuterosubstituted benzyl radicals, $C_6H_5CD_2$ and $C_6D_5CH_2$, have been investigated. The assignment of the IR bands of the benzyl radical and its deuteroanalogs to fundamental modes and a calculation of the valence force field have been performed. The obtained data give evidence of sp^2 hybridization of the methylene carbon atom and delocalization of the electron density between the ring and the CH_2 group, and are in good agreement with the planar structure of the radical.

Key words: benzyl radical; matrix isolation; IR spectroscopy, pyrolysis.

The benzyl radical $C_6H_5CH_2$ (1), the intermediate in many chemical reactions, has been studied by physical methods in detail.²⁻⁶ ESR experiments gave evidence⁷ that 60–70 % of the electron density is localized on the methylene carbon and 30–40 % is delocalized in the *o*- and *p*-positions of the benzene ring. This conclusion is in good agreement with the data of photoelectron spectroscopy⁸ and with quantum chemical calculations.⁹ However, reliable vibration parameters of this species have not been obtained until quite recently.

An investigation of radical 1 and its deuterosubstituted analogs $C_6H_5CD_2$ (2) and $C_6D_6CH_2$ (3) by matrix IR spectroscopy was performed in order to obtain more information about this species.

Radical 1 was generated in the gas phase by vacuum pyrolysis from two independent sources, *i.e.*, benzyl bromide (4) and dibenzyl (5). The pyrolysis products were frozen with excess argon on a CsI sublayer, and chilled to 12 K on a closed cycle cryogenic system. The IR spectra were recorded on IKS-24 and Hitachi—Perkin-Elmer-225 spectrophotometers. Pyrolysis of the starting compounds 4 and 5 was conducted at 1220-1270 K and 10^{-3} Torr (conversion ~80 %). The corresponding deuterated benzyl bromides C₆H₅CD₂Br (6) and C₆D₆CH₂Br (7) were used for preparing deuterated radicals 2 and 3. Compounds 6 and 7 were synthesized as follows:

$$C_{6}H_{5}COOC_{2}H_{5} \xrightarrow{\text{LiAID}_{4}} C_{6}H_{5}CD_{2}OH \xrightarrow{\text{HBr}} C_{6}H_{5}CD_{2}Br + H_{2}O,$$

$$6$$

$$C_{6}D_{6} + H_{2}CO \xrightarrow{\text{HBr}, ZnCl} C_{6}D_{5}CH_{2}Br.$$
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Along with the bands of stable molecules such as 4, toluene, HBr, and benzene the IR-spectrum of the matrix-isolated products of the thermal decomposition of 4 (Fig. 1,*a*) contained fourteen new bands at 3111 w, 3069 w, 1469 m, 1446 m, 1409 m, 1305 w, 1264 m, 1015 w, 948.1 v. w, 882.0 w, 762.0 v.s, 710.9 w, 667.0 s., and 465.0 s cm⁻¹. These bands decreased synchronously in intensity as the matrix was heated from 12 to 40 K. At the same time the intensity of the bands pertaining to toluene and dibenzyl 5 increased. The same set of bands, decreasing when the matrix was heated, was observed in the spectrum of the pyrolysis products of dibenzyl 5.

As was expected, these bands were absent in the spectra of the products of the thermal decomposition of 4 and 5 frozen on the sublayer without dilution with inert gas. It should be noted that under matrix heating and pyrolysis of 4 at higher pressure ($\sim 10^{-1}$ Torr), the generation of benzyl radical recombination product 5 is a minor process. In both cases toluene is the main product of the secondary reactions. The presence of only a small amount of 5 in the pyrolysis products of bromide 4 (the slight band at 754 cm⁻¹) even under increasing pressure in the heating zone is apparently accounted for by its propensity to dissociate to give radicals 1. Although under high pressure pyrolysis, the amount of radical 1 in

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Fig. 1. IR spectrum (Ar matrix, 12 K) of the pyrolysis products (1220 K, 10^{-3} Torr) of C₆H₅CH₂Br (*a*), C₆H₅CD₂Br (*b*), and C₆D₅CH₂Br (*c*). The absorption bands of the benzyl radicals are marked by arrows.

the reaction mixture decreased relative to toluene as the main secondary product, it remained quite noticeable. This allowed us to conclude that radical 1 has greater thermal and kinetic stability than other organic radicals (such as alkyl and allyl radicals).

Based on the information given above, the described processes can be represented by Scheme 1.

In order to better interpreting the vibration spectra of radical 1 we also investigated its deuterosubstituted analogs 2 and 3, stabilized in the inert matrix. In the IR spectrum of the pyrolysis products of bromide 6 (Fig. 1,b) there are eight bands belonging to radical 2: 3068, 1468, 1440, 1289, 1030, 880.4, 752.2, and 668.2 cm⁻¹. These bands decrease and disappear completely as the matrix is heated from 12 to 40 K. Similarly, in the spectrum of the products of the thermal decomposition of bromide 7 (Fig. 1,c) radical 3 was defined by bands at 2275, 1410, 1201.1, 821.3, 810.8, 759.0, 710.7, and 519.2 cm⁻¹.

Scheme 1



In both cases the formation of the suitable deuterotoluenes in the gas phase and in the secondary reactions when the matrix was heated, was observed.

On the basis of the isotopic shift and from a comparison with the vibrational spectra of different substituted benzenes we assigned the IR bands of radical 1 and its deuterosubstituted analogs 2 and 3 to the normal vibrations (Table 1). Theoretical calculation of the vibrational bands and valence force field were performed. The obtained results allowed us to make some conclusions about the nature of the structure of the benzyl radical.

The high value of the frequency of asymmetric C-H stretching $v_{as}(CH_2)$ equal to 3111 cm⁻¹ is evidence of sp^2 hybridization of the methylene carbon atom and is in good agreement with the planar structure of the radical. The increase in the exocyclic C-C bond stretching frequency from 1215 cm^{-1} in toluene to 1264 cm^{-1} in the benzyl radical and the simultaneous decrease in the C-C ring bond stretching frequencies (from 1496 and 1467 to 1469 and 1446 cm^{-1} , respectively) is ascribed to mutual influence of the radical center and the benzene ring and is the result of electron density delocalization in the π -system. The definition of the force field based on experimental data shows, that the carbon-carbon exocyclic bond force constant (5.5 mdyn $Å^{-1}$) is between the values for the normal C-C bond $(4.5 \text{ mdyn } \text{Å}^{-1})$ double C=Cand the bond (9.0 mdyn $Å^{-1}$). Its similarity to the corresponding force

Table 1. Interpretation of the vibrational spectra of the benzyl

 radical and its deuterosubstituted analogs

Sym-	Form	Frequency/cm ⁻¹		
metry	of vibra- tion	C ₆ H ₅ CH ₂	C ₆ H ₅ CD ₂	C ₆ D ₅ CH ₂
$\overline{A_1}$	v(CH)	3069	3068	2275
A ₁	v(CC)	1469	1468	
B_2	v(CC)	1446	1440	
$\bar{B_2}$	$\delta_r(CH)$	1305	_	
A ₁	v(CC) (exo)	1264	1289	1201
B_2	$\delta_{\rm r}({\rm CH})$			810.8
$\overline{B_2}$	$\delta_{r}(CH)$	1015		821.3
B ₁	$\rho_w(CH)$	882.0	880.4	759.0
$\hat{\mathbf{B}_1}$	$\rho_w(CH)$	762.0	752.2	
\mathbf{B}_{1}	$\rho_w(CH), \rho_t(CH)$) 667.0	668.2	519.2
B ₁	ρ _t (CC)	465.0		_
B ₂	v(CH ₂)	3111		
$\overline{A_1}$	$\delta(CH_2)$	1409	1030	1410
$\tilde{B_2}$	$\delta_r(CH_2)$	948.1		. <u> </u>
B ₁	$\rho_w(CH_2)$	710.9		710.7

constant in the allyl radical (5.8 mdyn $Å^{-1}$)¹⁰ confirms the similar nature of these species.

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