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The Isotope Effects in the Reactions of Phenylcarbene with Alcoholic Matrices

Hideo Tomioka,* Yasuji Ozaki, and Yasuji Izawa
Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514

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Synopsis. Product analysis studies on the reaction of phenylcarbene in deuterated alcoholic matrices at 77 K revealed that isotope effect on O–H (D) insertion is very small while substantial isotope effect was observed for C–H (D) insertion.

Recent reports from this[1–4] and other[5–8] laboratories have shown that the reactivity of arylcarbenes dramatically changes in rigid matrix at low temperature. The C–H insertion products increased drastically at lower temperature at the expense of characteristic singlet products (*vide infra*) and are believed to be derived from triplet arylcarbene *via* hydrogen atom abstraction and radical recombination. For example, we have found[1–4] in the reaction of arylcarbene with alcohol that the C–H insertion products increase dramatically at lower temperature at the expense of the OH insertion product. Recent kinetic studies of Platz[9,10] and Gasper[11] have demonstrated that the hydrogen atom abstraction from matrix is not a classical process but quantum mechanical tunneling in nature. There is little doubt that tunneling is often involved in hydrogen atom and proton transfer. It has been indicated[12] in the hydrogen atom abstraction by radicals that one of the characteristic phenomena for tunneling reaction is a very large kinetic isotope effect. For example, Ingold *et al.*[12] have observed k_H/k_D for the intramolecular hydrogen atom tunneling of 2,4,6-tri-*t*-butylphenyl radical is 1.3×10^4 at 123 K, while the maximum possible value for k_H/k_D for the simple rupture of a C–H/C–D bond is estimated to be 260 at 123 K. Similarly, Williams *et al.*[13] have reported that k_H/k_D is larger than 1.3×10^3 for intermolecular hydrogen atom abstraction by $CH_3\cdot$ from matrix at 110 K. Thus in order to obtain more precise insight into the mechanism of carbene reaction in matrix, it is quite important to investigate isotope effect on the product distribution. We wish to report here the product analysis studies on the reaction of phenylcarbene in deuterated alcoholic matrices at 77 K.

Results and Discussion

Degassed solutions of phenyldiazomethane (**1**) in methanol and its deuterated modifications were photolyzed at 77 K until all of **1** was destroyed. The product distributions were determined by GC and reported in Table 1. It is evident that isotope effect on O–H (D) insertion is very small but that there is a substantial isotope effect on C–H (D) insertion.

$$\underset{\mathbf{1}}{PhCH{=}N_2} \xrightarrow[-N_2 \atop 77\ K]{h\nu} \underset{\mathbf{2}}{[PhCH:]} \xrightarrow[MeOH]{} \underset{\mathbf{3}}{PhCH_2OMe} + \underset{\mathbf{4}}{PhCH_2CH_2OH} \qquad (1)$$

Table 1. Isotope effects in the reaction of phenylcarbene with isotopically labelled methanol at 77 K

Matrix	Yield/%[a)]	
	3	**4**
CH_3OH	40.8	26.2
CH_3OD	39.1	31.1
CD_3OD	64.6	9.1

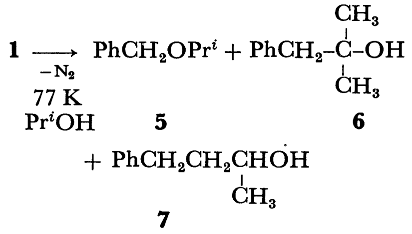
a) Other minor products (≈5%) detected in each run were toluene, bibenzyl, stilbenes, and aldehyde azine. Yield of these minor products was not altered by matrix.

Table 2. Isotope effects in the reaction of phenylcarbene with isotopically labelled 2-propanol at 77 K

Matrix	Yield/%[a)]		
	5	**6**	**7**
$(CH_3)_2CHOH$	15.3	52.7	11.9
$(CH_3)_2CDOH$	15.7	17.2	48.7
$(CD_3)_2CHOH$	20.4	50.5	7.3

a) See footnote a in Table 1.

Accepting the assumption that the relative yields of products are directly proportional to their relative rates of formation, k_H/k_D for O–H and C–H insertion can be calculated to be 1.2 and 5.6, respectively. A more instructive result is provided in a study of a series of isotopically labelled 2-propanols (see Table 2). Thus,



$$\mathbf{1} \xrightarrow[-N_2 \atop {77\ K \atop Pr^iOH}]{} \underset{\mathbf{5}}{PhCH_2OPr^i} + \underset{\mathbf{6}}{PhCH_2\text{–}\overset{CH_3}{\underset{CH_3}{C}}\text{–}OH} + \underset{\mathbf{7}}{PhCH_2CH_2\underset{CH_3}{CH}OH} \qquad (2)$$

β-C–H insertion product (**7**) increased dramatically in 2-propan-2-*d*-ol matrix while *α*-C–H insertion (**6**) became dominant in 2-propan-1,1,1,3,3,3-d_6-ol matrix. Thus, k_H/k_D for *α*-C–H and *β*-C–H insertion can be similarly calculated to be 3.1 and 2.2, respectively.

The lack of isotope effect on O–H (D) insertion along with the kinetic observation[9,10,17] that retardation of the decay rate of triplet arylcarbene is not significant in alcohol-*hydroxyl-d* matrix indicates that abstraction of hydrogen from an O–H bond of alcohol by triplet carbene hardly occurs in matrix. This is quite reasonable in light of the large O–H bond dissociation energy (103 kcal/mol).[14] Most of ethers are then derived from singlet carbene even in rigid matrix.

Considerable isotope effect on C–H insertion supports the idea that C–H insertion products are arising from triplet carbene, presumably *via* the abstraction-recombination mechanism. It is somewhat surprising, however, to note that the observed C–H isotope effect is not so large as to prevent the formation of C–D insertion products. In their studies of isotope effect on H atom tunneling, Williams *et al.*[13] have shown that main decay pathways of $CH_3\cdot$ radicals change from H atom abstraction to recombination with other $CH_3\cdot$ radicals in going from CH_3NC to CD_3NC matrix because of large kinetic isotope effect. No appreciable increase in such recombination products as azine and stilbene even in CD_3OD matrix indicates that decay pathways of triplet phenylcarbene are primarily D atom abstraction even in the perdeutrated solvent. The result is consistent with the kinetic observation that isotope effects with arylcarbenes are much more modest (*vide infra*).[9,10] This is partly attributable to a matrix-site problem. The rate of a hydrogen atom tunneling process is dependent upon not only the barrier height but also width: the barrier height is the classical activation energy but the barrier width is the distance that the hydrogen atom must tunnel from matrix molecule to the arylcarbene. The kinetic studies[9–11] show that decay of triplet carbene does not follow the simple pseudo first order kinetics. Such nonexponential decay has been attributed to the effects of different matrix sites offering various degrees of freedom for reaction. The findings[15] that arylcarbene generated in rigid isobutane matrix results in dramatic increase in primary C–H insertion over tertiary have been interpreted in terms of such effects of different matrix sites. In the early stages of the reaction, the reactive sites are quickly depleted while the remaining carbenes are in less reactive sites. The matrix isotope effects are found[9] to vary with matrix sites. Thus, for diphenylcarbene in toluene-d_8, matrix rate constants $k_H/k_D=6.92$ at 77 K, but initial rate constants (10% decay) $k_H/k_D=23$ at 77 K. The bulk chemistry of low temperature samples must reflect sum of those carbenes located in various sites.[16]

Experimental

Materials. Phenyldiazomethane was prepared as described in the literature[17] immediately before use. All deuterated methanols were purchased from E. Merck and used without purification. 2-Propan-2-*d*-ol was prepared by $LiAlD_4$ (E. Merck) reduction of CH_3COCH_3 and 2-propan-1,1,1,3,3,3-d_6-ol was prepared $LiAlH_4$ reduction of CD_3COCD_3 (E. Merck) according to literature procedures.[18] The undeuterated solvents were distilled over anhydrous $CaSO_4$ prior to use. Authentic samples of phenylcarbene adducts with alcohols (**3**—**7**) were synthesized as described in the literature.[19]

Low Temperature Irradiations and Product Analyses. All irradiations were carried out with a Halos 300-W high-pressure mercury lamp with a water-cooled jacket. In a typical procedure, 0.005 mmol of the freshly prepared diazomethane was added to a 2.0 ml of alcohol in Pyrex tubes. Sample tubes were sealed under vacuum after three freezethaw cycles, immersed in a trasparent Dewar filled with liquid nitrogen, and irradiated until all of the diazomethane was destroyed. Product identifications were established by GC or GC-MS comparisons using authentic samples. Product distributions were conveniently determined on 2.0 m 5% OV-17 column at 120 °C.

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