

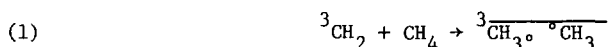
# TUNNELING PARAMETERS FOR THE HYDROGEN ATOM ABSTRACTION REACTIONS OF DIPHENYLCARBENE IN A LOW TEMPERATURE TOLUENE MATRIX

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**Abstract:** *Tunneling reaction rate constants of diphenylcarbene in a toluene matrix can be fit by an asymmetric Eckart barrier. The barrier heights are in good agreement with theory.*

The absolute rate constants of several solution phase carbene reactions have been reported. These studies have focused on the reactions of aryl carbenes with alcohols or unsaturated species, particularly alkenes, dienes, and ketones.<sup>1</sup> To the best of our knowledge no solution rate constant for the elementary process of hydrogen or deuterium atom abstraction by a triplet carbene has been reported.

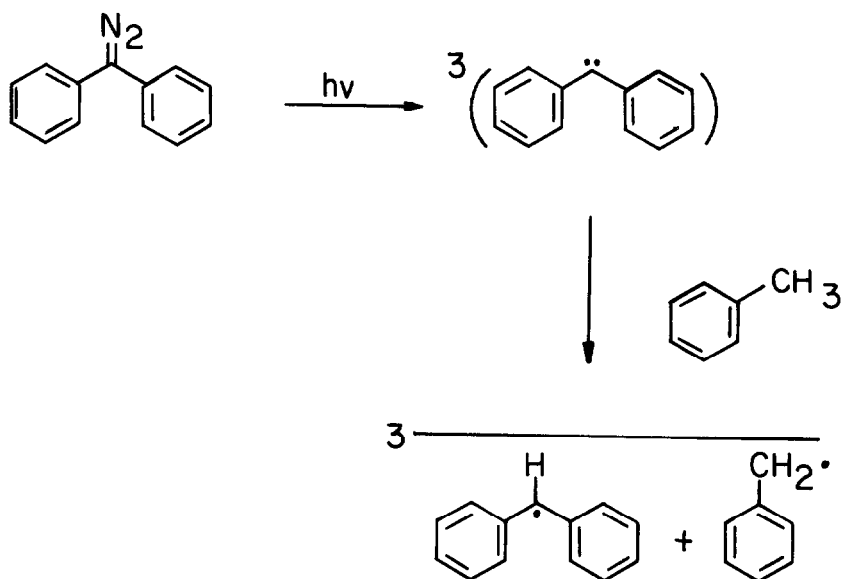


This can be attributed to the relatively slow rate of the abstraction process which complicates the kinetic analysis.<sup>2</sup> Indeed,<sup>3</sup> the gas phase rate constant for reaction (1) is less than  $5 \times 10^{-14} \text{ cm}^3/\text{molecule s}^{-1}$ . *Ab initio* molecular orbital calculations of reaction (1) predict a sizable activation energy (~7 kcal/mole) for reaction.<sup>4</sup>

There now exists a substantial amount of data pertaining to the matrix chemistry of aromatic carbenes. The groups of Moss and Tomioka have found that hydrogen atom abstraction from the solvent matrix is the dominant chemical reaction of triplet carbenes at 77K.<sup>5</sup> This poses the question of how a sluggish reaction in solution at room temperature manages to proceed at a useful rate in a matrix at 77K. ESR kinetic studies of triplet aryl carbenes in matrices indicate that the answer to the preceding question is that the abstraction process in matrices proceeds via quantum mechanical hydrogen atom tunneling.<sup>6</sup> The tunneling contribution to the classical carbene hydrogen atom abstraction is expected to be small in solution at elevated temperatures (~273K). In a low temperature (77-110K) polycrystalline matrix the rate of the classical reaction is essentially zero. The tunneling reaction rate although small in the matrix, is much larger than that of the classical process. In this work we report the energy barriers to hydrogen atom abstraction of diphenylcarbene obtained from the analysis of tunneling rate constants.

A degassed solution of diphenyldiazomethane (0.1 M) in toluene was cooled to between 77 and 105K in the cavity of an ESR spectrometer. The resulting polycrystalline matrix was photolyzed for 100 seconds to produce the known triplet ESR spectrum of diphenylcarbene<sup>7</sup>. The decay kinetics of the carbene was measured immediately upon shuttering the light source and was followed at ~1100 Gauss. Previous work of Platz and Gaspar<sup>6,8</sup> has demonstrated the problems associated with sites of differing reactivity in the matrix. The aforementioned experimental conditions employed, coupled with the analysis of initial decay rates, minimized the matrix site problems and gave the pseudo first order rate constants listed in Table 1. The reaction rates presented herein are somewhat larger than those reported by Gaspar. This is primarily due to

the large difference in diazo compound concentration of the two studies which changes the reactivity of the matrix sites.



Tunneling rate constants were calculated assuming an asymmetric Eckart potential surface of known barrier height ( $V$ ), barrier width parameter ( $b$ ), and zero point energy (see Figure).<sup>9</sup> The zero point energy was calculated from the symmetric stretching vibration of the matrix carbon-hydrogen bond (4.172 kcal/mole). The enthalpy of reaction does not significantly affect the tunneling rate constant provided the reaction is exothermic. Following the theoretical procedures of LeRoy, Murai and Williams, the two unknown tunneling parameters ( $V$  and  $b$ ) were obtained by a non-linear least squares best fit of the calculated to the experimental rate constants.<sup>10</sup> The theoretical treatment is a one dimensional model which makes use of tunneling corrected transition state theory with coupling to the matrix. The calculated tunneling rate constants are listed in Table 1 along with the barrier heights and widths. The agreement between the calculated and observed rates is comparable to that found by LeRoy for the matrix reactions of methyl radical.<sup>10</sup> After correcting for the zero point energy, the calculated activation energy for the classical hydrogen atom abstraction reaction of diphenylcarbene is 8.7 kcal/mole. This is consistent with the relatively slow rate of triplet hydrogen atom abstraction processes in solution, and remarkably similar to the activation energy for hydrogen atom abstraction by triplet methylene as calculated by Schaefer.<sup>4</sup>

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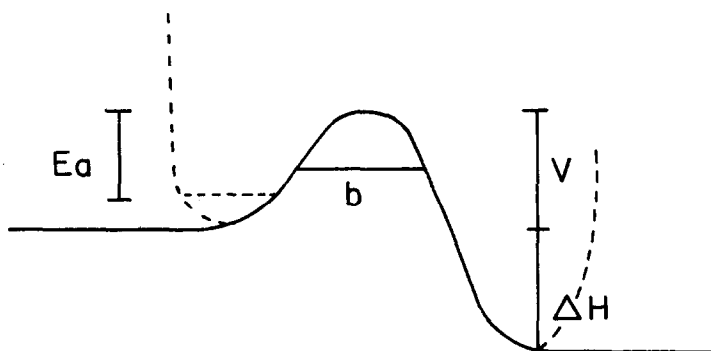
Table 1. Calculated and Experimental Tunneling Initial Rate Constants of Diphenylcarbene in Toluene in  $\text{S}^{-1}$ .

Temp ( K )	k (exp)	k (calc)
77	0.00063	0.00073
95	0.0046	0.0036
99	0.0067	0.0060
103	0.0095	0.011
106	0.017	0.018

$$V = 12.9 \text{ kcal/mole}$$

$$b = 1.25 \text{ \AA}$$

$$E_a = 8.7 \text{ kcal/mole}$$



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