

Absolute Rate Constants for Decarbonylation of Phenylacetyl and Related Radicals

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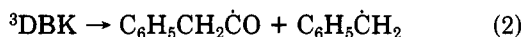
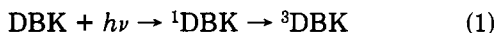
The rate constants and Arrhenius parameters for decarbonylation of phenylacetyl ($C_6H_5CH_2\dot{C}O$), phenylmethylacetyl ($C_6H_5CHCH_3\dot{C}O$), and phenyldimethylacetyl [$C_6H_5C(CH_3)_2\dot{C}O$] radicals in isooctane have been determined by laser flash photolysis. The variation of the rate constant for decarbonylation follows the pattern expected from radical stabilities, but the activation energies do not. It is proposed that previously unrecognized conformational restrictions may be significant in determining decarbonylation rates.

Introduction

The type I α cleavage of ketones is an extensively studied system whose primary photochemical step (typically homolytic cleavage of a CO-C bond in either S_1 or T_1 of the ketone) is well understood from the standpoint of quantitative structure reactivity relations.¹ The rate of decarbonylation of the acyl fragment (produced in the primary photochemical step) relative to other reactions often determines the structure of overall products produced in type I reactions, especially in the case of cyclic ketones, and has been found to be an important parameter in determining the observed polarization in CIDNP spectra.² It has recently been suggested that conformations³ of the fragments produced by type I cleavage may be important in determining product structures and the rate of intersystem crossing of the radical pair (or diradical). In addition to its importance in photochemical process and the chemistry of radical pairs containing acyl fragments, the rate of decarbonylation of acyl radicals is of broad significance to radical chemistry and have considerable potential in the development of useful radical clocks.⁴

The photolysis of dibenzyl ketone (DBK) has recently served as a paradigm system for the investigation (1) of magnetic isotope and magnetic field effects on reactions of radical pairs,⁵ (2) of microenvironments such as micelles,⁶ and (3) of reactions on solid surfaces.⁷ Therefore, it was of interest to measure the rate and Arrhenius parameters of decarbonylation of the phenylacetyl radical ($C_6H_5CH_2\dot{C}O$, 1) and its methylated derivatives phenylmethylacetyl ($C_6H_5CHCH_3\dot{C}O$, 2) and phenyldimethylacetyl [$C_6H_5C(CH_3)_2\dot{C}O$, 3] radicals.

For the purposes of this report, the mechanism of photolysis of DBK⁸ is summarized by eq 1-5. We have



(1) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA; 1978, p 528 ff.

(2) Lehr, G. F.; Turro, N. J. *Tetrahedron* 1981, 37, 3411.

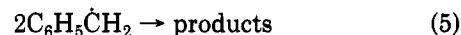
(3) de Kanter, F. J. J.; Kaptein, R. *J. Am. Chem. Soc.* 1982, 104, 4759. Doubleday, C. E. *Chem. Phys. Lett.* 1981, 79, 375. 1981, 77, 131. 1979, 64, 67.

(4) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* 1980, 13, 317.

(5) Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* 1980, 13, 369. Turro, N. J. *Pure Appl. Chem.* 1981, 53, 259.

(6) Turro, N. J.; Gratzel, M.; Braun, A. J. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 675.

(7) Baretz, B. H.; Turro, N. J. *J. Am. Chem. Soc.* In press.



employed time-resolved laser flash spectroscopy⁹ to monitor step 3, and the analogous step for 2 and 3. Pulsed laser photolysis of DBK (and also DMDBK and TMDBK in Table I) produced a transient absorption at 317 nm which was assigned to the benzyl radical. An initial jump in transient absorption occurred within the time period of the laser pulse and was followed by a measurable first-order growth of absorption. We interpret these results to mean that step 2 occurs in less than 10^{-8} s so that benzyl radical appears "immediately" after the pulse, and that step 3 is responsible for a slower production of benzyl radicals. Thus, analysis of the growth portion of the time-resolved absorption will yield, k_{CO} , the rate constant for decarbonylation of radical 1. In nonviscous homogeneous solution, the recombination step 4 is not a significant contributor to the decay of benzyl radicals. However, step 5, all bimolecular pathways for disappearance of benzyl radicals, becomes significant at high laser powers (~ 100 mJ/cm²). At lower laser power (~ 10 -20 mJ/cm²) the first-order growth of benzyl radical absorption led to an initially flat plateau (cf. Figure 1) followed by second-order decay. The growth portion of the absorption was analyzed according to eq 6, where OD_t is the optical density at 317

$$\ln(OD_t - OD_\infty) = -k_{CO}t + C \quad (6)$$

nm at time t and OD_∞ is the optical density at $t = \infty$. The growth portion of the transient absorption approaches, but does not reach, a value of twice the OD immediately following the pulse.¹⁰

Our results for DBK are summarized in Table I, along with results for comparable data obtained by laser flash photolysis of DMDBK and TMDBK to yield radicals 2 and 3, respectively.

The rate constant k_{CO} at 25 °C was determined to be 5×10^6 s⁻¹, a value consistent with an upper limit of 10^7 s⁻¹ imposed by a CIDNP study² in C_6D_6 , but lower than an estimate ($\sim 10^8$ s⁻¹) based on extrapolation of ESR data.¹¹

(8) Engel, P. S. *J. Am. Chem. Soc.* 1970, 92, 6074. Robbins, W. K.; Eastman, R. H. *Ibid.* 1970, 92, 6076.

(9) Lambda Physik excimer laser (248 nm, 15 ns), cf. Turro, N. J.; Aikawa, M.; Butcher, J. *J. Quantum Electron.* 1980, QE-16, 1218.

(10) Various factors could be the basis for this observation (e.g., photoinduced decarbonylation of phenylacetyl radicals during the laser pulse, absorption due to phenylacetyl radicals, etc.); however, such effects would not be expected to interfere with the interpretation of the transient kinetics.

(11) Brunton, G.; McBay, H. C.; Ingold, K. U. *J. Am. Chem. Soc.* 1977, 99, 4447.

TABLE I: Arrhenius Parameters for Decarbonylation of Acyl Radicals

radical	$\lambda_{\text{obsd}},^a$ nm	temp range, ^b K	$\log A,^c$ s ⁻¹	$E_a,^c$ kcal/mol ⁻¹	$k_{-\text{CO}}^{(300\text{K})},^d$ s ⁻¹
PhCH ₂ CO ^e	317	263-313 (25)	11.2 ± 0.4	6.1 ± 0.6	6.4 × 10 ⁶
PhCH(CH ₃)CO ^f	319	223-251 (10)	12.2 ± 0.7	6.2 ± 0.7	4.9 × 10 ⁷
PhC(CH ₃) ₂ CO ^g	322	178-203 (8)	11.2 ± 0.6	4.1 ± 0.5	1.5 × 10 ⁸

^a Observation wavelength for growth of product radical (4-nm bandwidth). ^b Number in parentheses is the number of temperatures at which measurements were made. ^c Errors quoted represent two standard deviations or 95% confidence limits. ^d Rate constants determined from Arrhenius parameters. ^e The precursor ketone is dibenzyl ketone (DBK). ^f The precursor ketone is α, α' -dimethyldibenzyl ketone (DMDBK). ^g The precursor ketone is $\alpha, \alpha, \alpha', \alpha'$ -tetramethyldibenzyl ketone (TMDBK).

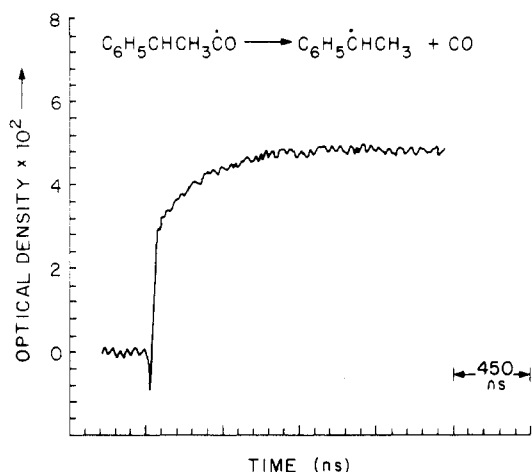


Figure 1. Typical transient trace showing growth of the PhCH(CH₃) radical following pulsed laser photolysis of DMDBK. $\lambda_{\text{obsd}} = 319$ nm, temperature = 235 K.

The rate constants for decarbonylation are in the expected order based on radical stability of the product 3 > 2 > 1; however, the Arrhenius parameters reveal that

the activation energies for decarbonylation of 1 and 2 are experimentally identical and distinctly larger than the activation energy for decarbonylation of 3. Thus, it appears that there may be a previously unrecognized feature of the phenylmethylacetyl radical 2 that leads to an unexpectedly large activation energy. This possibility is of interest because of recent results which point to the role of conformations in controlling certain aspects of the reactions of diradicals produced by type I cleavage of cyclic ketones.³

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Supplementary Material Available: Tables II, III, and IV provide detailed kinetic data (3 pages). Ordering information is available on any current masthead page.