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LETTERS

Absolute Rate Constants for the Decarbonylation of the Phenylacetyl Radical[1]

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The rate of α scission of the phenylacetyl radical has been determined by laser flash photolysis in isooctane, methanol, and tetrahydrofuran. There is no significant solvent effect on the rate. In isooctane, the rate constant for decarbonylation can be represented by $\log (k/\mathrm{s}^{-1}) = (12.0 \pm 0.3) - (6.9 \pm 0.4)/2.3RT$ kcal/mol.

Although there have been relatively few measurements of the absolute rates of decarbonylation of acyl radicals, $R\dot{C}O$, it is clear that these rates are highly dependent on the degree of stabilization of the radical R· (see Table I).[3-9]

$$R\dot{C}O \rightarrow R\cdot + CO \qquad (1)$$

Since all $R\dot{C}O$ are σ radicals it would be expected that their rates of formation by, for example, H-atom abstraction from RCHO by a specific free radical will be similar and that they will exhibit very similar reactivities in their intermolecular reactions. Reaction 1 can therefore provide a series of "clocks"[10] of general utility which can be used to determine the rates with which $R\dot{C}O$ radicals undergo intermolecular reactions.

Phenylacetyl undergoes the fastest known decarbonylation[9] and, for many purposes, it is therefore the most useful $R\dot{C}O$ clock. Unfortunately, the rate constant for decarbonylation of this radical has been measured at only one temperature (see Table I).[11] The growing use of this reaction as a general probe of kinetic processes in homogeneous and in micellar solutions[12-14] makes a reliable determination of its kinetic parameters in nonpolar, polar, and hydrogen-bonding solvents of considerable importance. We now report a kinetic study of this reaction in isooctane, tetrahydrofuran (THF), and methanol. The $C_6H_5CH_2\dot{C}O$ radicals were generated by laser flash photolysis with the pulses from an excimer laser (308 nm, ~5 ns, up to 80 mJ) and dibenzyl ketone (1–5 mM) as the substrate. The

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(11) A CIDNP study[12] has yielded $k_1 \leq 10^7$ s^{-1} for $C_6H_5CH_2\dot{C}O$ at 304 K.

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TABLE I: Kinetic Data for Acyl Radical Decarbonylations

radical	solvent	temp range, K	$\log A_1$, s^{-1}	E_1, kcal/mol	k_1^{300K},[a] s^{-1}	ref
$C_6H_5\dot{C}O$	gas phase	614-667	14.6 ± 0.5	29.4 ± 1.8	1.5×10^{-7}	3
$CH_3\dot{C}O$	gas phase	508-568	10.3	15.0	0.23	4
$CH_3\dot{C}O$	gas phase	326			(19.1 ± 3.0)	5
$CH_3CH_2\dot{C}O$	gas phase	303-353	13.32	14.7	4.0×10^2	6
$CH_3CH_2\dot{C}O$	gas phase	238-378	12.77	14.4	1.9×10^2	7
$(CH_3)_3C\dot{C}O$	methylcyclopentane	203-263	11.9	9.3	1.3×10^5	8
$C_6H_5CH_2\dot{C}O$	cyclopropane	157			(9×10^2)	9
$C_6H_5CH_2\dot{C}O$	benzene-d_6	304			$(\leqslant 10^7)$	12
$C_6H_5CH_2\dot{C}O$	isooctane	245-331	12.0 ± 0.3	6.9 ± 0.4	9.1×10^6	this work
$C_6H_5CH_2\dot{C}O$	methanol	259-302	12 ± 1	7.3 ± 1.3	5.2×10^6	this work
$C_6H_5CH_2\dot{C}O$	THF	291			(5.05×10^6)	this work
$C_6H_5CH_2\dot{C}O$	THF	314			(1.08×10^7)	this work

[a] Values calculated from Arrhenius parameters except for those given in parentheses which correspond to the measured value of k_1 at the temperature indicated in column 3.

benzyl radical concentration, which was monitored at 317 nm, showed an instantaneous "jump" (due to reaction 2), which was followed by a slower first-order growth to a plateau approaching, but somewhat less than, twice the height of the initial jump (reaction 3). Analysis of the

$$(C_6H_5CH_2)_2CO \xrightarrow[308\ \mathrm{nm}]{h\nu} C_6H_5\dot{C}H_2 + C_6H_5CH_2\dot{C}O \qquad (2)$$

$$C_6H_5CH_2\dot{C}O \rightarrow C_6H_5\dot{C}H_2 + CO \qquad (3)$$

growth portion of these traces yielded rate constants for phenylacetyl decarbonylation. The results are summarized in Table I, full kinetic data being available as supplementary material.

A few problems that were encountered in trying to extend our measurements beyond those listed in Table I are worth noting. Problems due to luminescence from trace impurities in the solvents were particularly acute in these systems. All experimental traces were corrected by subtracting this luminescence. In THF these problems limited our measurements to only two temperatures. An attempt to generate $C_6H_2CH_2\dot{C}O$ by 308-nm photolysis of phenylacetyl chloride was unsuccessful, as was an attempt to measure k_1 for $(CH_3)_3C\dot{C}O$ generated by the 308-nm photolysis of di-*tert*-butyl ketone. At ambient temperatures the decarbonylation of the pivaloyl radical was too slow[8] for study by our technique.

The rate of α scission of the phenylacetyl radical is invariant (within our limits of experimental error) in solvents which have widely different properties.[15] Since the same should apply to other acyl radicals, the utility of decarbonylations as acyl radical clock reactions should be greatly increased.

In conclusion, we note that the preexponential factor of $10^{12.0}$ s^{-1} for reaction 3 appears to be reasonable since the formation of a benzyl radical from phenylacetyl requires that one internal rotation become at least partially "frozen" in the transition state. Undoubtedly some of the previously reported preexponential factors listed in Table I are too small.

Supplementary Material Available: Tables II and III giving detailed kinetic data (2 pages). Ordering information is given on any current masthead page.

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[15] In contrast, the rate of β scission of *tert*-butoxyl to form acetone and a methyl radical is dramatically greater in hydrogen-bonding solvents,[16-18] or in the presence of compounds which complex with acetone,[19] than in nonpolar solvents.

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