putative intermediates in solution. Rearrangement or elimination with loss of nitrogen from **3** and **4** does not occur under our solvolysis conditions.[19] Therefore, if these α-azido carbocations *are* intermediates in the Schmidt reaction, then, under neutral solvolysis conditions, the reaction of water with **3** and **4** to give the benzaldehydes **1** and **2** is much faster than the step(s) which give the Schmidt-type products ($k_{hyd} \gg k_{Schmidt}$).

We conclude that if the Schmidt reaction proceeds through iminodiazonium ions, then either their formation from carbonyl compounds is reversible in concentrated acid or the decrease in the activity of water in these solutions leads to a change in rate-determining step, so that $k_{Schmidt} \gg k_{hyd}$.[20] Calculations suggest that equilibration of the cis and trans isomers of iminodiazonium ions cannot proceed by inversion at nitrogen, but must involve reversible hydration of the iminodiazonium ion to give the azidohydrin, followed by dehydration to give the geometrical isomer.[16]

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[19] Within the limits of detection, the reactions of **1** and **2** were shown by UV spectroscopy and HPLC analysis to give only the corresponding benzaldehydes.[11]

[20] The reactivities of oxocarbenium ions toward water in 60% and 90% sulfuric acid are ~10^4- and ~10^{10}-fold lower, respectively, than in dilute aqueous solution: McClelland, R. A.; Ahmad, M. *J. Am. Chem. Soc.* **1978**, *100*, 7031-7036.

First Direct Detection of Transient Organic Free Radicals in Solution by Time-Resolved Infrared Spectroscopy. Kinetic Studies on Some Acyl Radicals[1]

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Acyl radical chemistry is an extremely active field at present,[3] but both absolute reactivities[4] and C=O stretching frequencies[6] of these species have been virtually unexplored in solution. Appropriate kinetic data would be of immeasurable value to synthetic chemists designing new radical chain reactions. However, it would not be easy to apply conventional laser flash photolytic (LFP) techniques since acyl radicals such as, for example, the benzoyl radical[3b,c] have only a weak absorption in the UV and this absorption occurs in the same wavelength range as absorptions from many other transient species. We have overcome these difficulties by a novel application of LFP using time-resolved infrared (TRIR) studies to detect and monitor some representative acyl radicals, RC$^{\bullet}$=O, in solution. This work represents the first direct observation of a transient organic free radical in solution by LFP/TRIR.[10]

Table I. LFP/TRIR Generation and Identification of Some Acyl Radicals

ketone	acyl radical	$\nu_{C=O}$,[a] cm^{-1}
$CH_3CH_2COCH_2C_6H_5$	$CH_3CH_2C^{\bullet}{=}O$	1859
$(CH_3)_2CHCOCH(CH_3)_2$	$(CH_3)_2CHC^{\bullet}{=}O$	1853
$(CH_3)_3CCOC(CH_3)_3$	$(CH_3)_3CC^{\bullet}{=}O$	1848
$C_6H_5COC(CH_3)_3$	$C_6H_5C^{\bullet}{=}O$	1828

[a] Estimated peak position. Error ±2 cm^{-1}.

Table II. Kinetic Data for Some Benzoyl Radical Reactions at Room Temperature (24 ± 1 °C)

quencher	product	k, M^{-1} s^{-1}
CCl_4	$C_6H_5C(O)Cl$	5.6×10^4
CCl_3Br	$C_6H_5C(O)Br$	2.2×10^8
C_6H_5SH	C_6H_5CHO	4.7×10^7

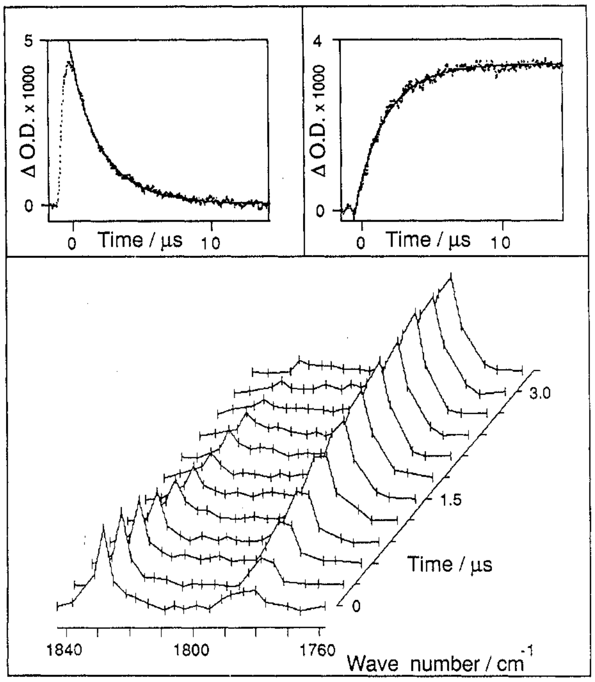

Figure 1. Time-resolved IR spectrum recorded during reaction of the benzoyl radical with 0.003 M CCl_3Br. Top left insert shows decay of the 1828-cm^{-1} band (benzoyl), and top right insert shows the growing in of the 1780-cm^{-1} band (benzoyl bromide) which was monitored at 1784 cm^{-1}.

The acyl radicals were generated by 308-nm LFP induced α-cleavage of appropriate ketones,[11] reaction 1, in Ar-saturated *n*-hexane as solvent using a calcium fluoride cell and a flow system at room temperature.[12] From each ketone (see Table I), only

$$RCOR' \xrightarrow[308\ nm]{h\nu} RC^{\bullet}{=}O + R'^{\bullet} \qquad (1)$$

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[1] Issued as NRCC No. 32319.

[2] NRCC Research Associate, 1989-1990.

[3] For some recent examples, see: (a) Boger, D. L.; Mathvink, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 4003-4008, 4008-4011. Crich, D.; Fortt, S. M. *Tetrahedron* **1989**, *45*, 6581-6598. Bachi, M. D.; Bosch, E. *Heterocycles* **1989**, *28*, 579-583. Bachi, M. D.; Denenmark, D. *Heterocycles* **1989**, *28*, 583-588. Mestre, F.; Tailhan, C.; Zard, S. Z. *Heterocycles* **1989**, *28*, 171-174. (b) Weir, D.; Ajayaghosh, A.; Muneer, M.; George, M. V. *J. Photochem. Photobiol., A: Chem.* **1990**, *52*, 425-437. (c) Fischer, H.; Baer, R.; Hany, R.; Verhoolen, I.; Walbiner, M. *J. Chem. Soc., Perkin Trans. 2* **1990**, 787-798.

[4] The only previously reported absolute rate constants for reaction of an acyl radical with a compound in solution are a value of 4.8×10^5 M^{-1} s^{-1} at 25 °C for pivaloyl addition to acrylonitrile (obtained by a steady-state EPR technique),[5] and a value of 2.0×10^8 M^{-1} s^{-1} for the reaction of benzoyl with oxygen (obtained by laser flash photolysis with UV-visible detection).[3b]

[5] Jent, F.; Paul, H.; Roduner, E.; Heming, M.; Fischer, H. *Int. J. Chem. Kinet.* **1986**, *18*, 1113-1122.

[6] IR data on related RC$^{\bullet}$=O radicals appear to be limited to the gaseous phase (R = H, F) and to solid matrices (R = H, F, Cl, CH_3, HO).[7,8]

[7] (a) Jacox, M. E. *J. Phys. Chem. Ref. Data* **1984**, *13*, 945-1068. (b) See also: Jacox, M. E. *J. Chem. Phys.* **1988**, *88*, 4598-4607. Brown, J. M.; Dumper, K.; Lowe, R. S. *J. Mol. Spectrosc.* **1983**, *97*, 441-448. McKellar, A. R. W.; Burkholder, J. B.; Orlando, J. J.; Howard, C. J. *J. Mol. Spectrosc.* **1988**, *130*, 445-453.

[8] Values of $\nu_{C=O}$ are markedly dependent on the matrix, e.g., for $CH_3C^{\bullet}{=}O$, $\nu_{C=O}$ ranges from 1796 cm^{-1} in a CO_2 matrix[9] to 1842 and 1875 cm^{-1} in argon matrices.[7a]

[9] Bennett, J. E.; Graham, S. C.; Mile, B. *Spectrochim. Acta* **1973**, *29A*, 375-383.

[10] To date, only one family of transient organic molecules has been detected in solution by LFP/TRIR; see: Li, Y.-Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 8092-8098. For the first study of organic free radical kinetics using LFP/TRIR, see: Neville, A. G.; Brown, C. E.; Rayner, D. M.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1989**, *111*, 9269-9270.

[11] Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 13.2.

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a single transient absorption was formed within the response time of the detection system, in the 1750–1880-cm^{-1} region of the IR spectrum. We assign these IR bands to the acyl radicals indicated in Table I on the basis of their carbonyl stretching frequencies,[6-9] their kinetic behavior, and the identification of the expected reaction products which grow in at the same rate as the radicals decay.

Under our experimental conditions, the acyl radical IR absorptions decayed within microseconds with kinetics that were first order for pivaloyl but were predominantly second order for the other three acyl radicals (which presumably decay largely by radical–radical recombination). The pivaloyl radical is known to undergo a relatively rapid decarbonylation, reaction 2.[5,13] By

$$(CH_3)_3CC^{\bullet}{=}O \rightarrow (CH_3)_3C^{\bullet} + CO \tag{2}$$

using a static system from which all traces of oxygen (vide infra) were removed by several freeze–pump–thaw cycles, we found the rate constant for decay of the pivaloyl radical to be 7×10^5 s^{-1}, independent of the laser dose. We equate this rate constant with k_2 (see footnote 14) and note that it is in satisfactory agreement with an indirectly determined value of 4.4×10^5 s^{-1} at 25 °C which was obtained by Fischer and co-workers[5,15] using an EPR method.

The rates of decay of the transient IR signals can be increased by the addition of compounds (quenchers) which might be expected to react with acyl radicals, e.g., CCl_4, CCl_3Br, C_6H_5SH, and O_2. By a careful analysis of the decay traces found with different concentrations of added quenchers (including fitting the experimental data with mixed (pseudo) first- and second-order kinetics), kinetic data were obtained as illustrated for the benzoyl radical in Table II. The loss of the 1828-cm^{-1} band of benzoyl was matched for CCl_4 and CCl_3Br (see Figure 1) by the growth of new carbonyl absorptions which occurred at the known frequencies for the expected products, viz., $C_6H_5C(O)Cl$ and $C_6H_5C(O)Br$, respectively. However, the rate constant for reaction with C_6H_5SH[16] could only be determined from the decay of the benzoyl radical since absorption from the expected product, C_6H_5CHO, was masked by absorption of the starting ketone. With oxygen as the quencher, a new absorption grows in at 1820 cm^{-1}, which we assign to the benzoylperoxyl radical.[17]

From the known extinction coefficient of $C_6H_5C(O)Br$ we estimate that the extinction coefficient for the benzoyl radical at 1828 cm^{-1} has a value of ca. 1300 M^{-1} cm^{-1}.

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Registry No. $CH_3CH_2COCH_2C_6H_5$, 1007-32-5; $(CH_3)_2CHCOCH(CH_3)_2$, 565-80-0; $(CH_3)_3CCOC(CH_3)_3$, 815-24-7; $C_6H_5COC(CH_3)_3$, 938-16-9; $CH_3CH_2\dot{C}{=}O$, 15843-24-0; $(CH_3)_2CH\dot{C}{=}O$, 35586-36-8; $(CH_3)_3C\dot{C}{=}O$, 50694-27-4; $C_6H_5\dot{C}{=}O$, 2652-65-5.

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(14) We rule out any significant contribution to the measured first-order rate constant from an attack on the *n*-hexane solvent because the other three acyl radicals decay with second-order kinetics. We estimate that at room temperature the reaction $RC^{\bullet}{=}O + C_6H_{14} \rightarrow RCHO + C_6H_{13}^{\bullet}$ must have $k \le 5 \times 10^3$ M^{-1} s^{-1}.

(15) An earlier value[13b] of 1.2×10^5 s^{-1} at 25 °C in methylcyclopentane would appear to have been in error. A third value of 3.5×10^5 s^{-1} derived from indirect CIDNP measurements[13c] is in fair agreement with the latest result.[5]

(16) The large magnitude of this rate constant is somewhat surprising since thiyl radicals are believed to abstract hydrogen from aldehydes rather efficiently. See: Walling, C. *Free Radicals in Solution*; Wiley and Sons Inc.: New York, 1957; pp 325–326.

(17) For the matrix-trapped (and possibly "perturbed") $HC(O)OO^{\bullet}$ radical, $\nu_{C=O}$ has been reported to be 1790 cm^{-1}.[18]

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η^2-Silanimine Complexes of Zirconocene: Synthesis, Structure, and Reactivity of $Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(PMe_3)$

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Silanimines ($R_2Si{=}NR'$) are one of several classes of very reactive species exhibiting unsaturation at silicon.[2] Several examples of stable silanimines in which the Si=N bond is protected by bulky substituents have been isolated.[3] Recently, there has been interest in stabilizing unsaturated silicon species such as silylenes ($:SiR_2$),[4] silenes ($R_2Si{=}CR'_2$),[5] and disilenes ($R_2Si{=}SiR'_2$)[6] by coordination to transition metals. We now report the synthesis, structure, and reactivity of $Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(PMe_3)$ ($Cp \equiv \eta^5\text{-}C_5H_5$), the first example of a metal silanimine complex.

The synthetic strategy employed (Scheme I) involves formation of the unsaturated fragment by β-hydrogen abstraction and loss of alkane, in analogy to previously reported syntheses of organic imine complexes.[7] The amido complex $Cp_2Zr(H)(N^tBuSiMe_2H)$ (**1**) is prepared by metathesis of $[Cp_2ZrHCl]_n$ with $LiN^tBuSiMe_2H{\cdot}THF$.[8] Treatment of **1** with MeI yields the iodide $Cp_2Zr(I)(N^tBuSiMe_2H)$ (**2**) and methane. Alkylation of **2** with $LiCH_2SiMe_3$ in benzene solution generates the (trimethylsilyl)methyl derivative, $Cp_2Zr(CH_2SiMe_3)(N^tBuSiMe_2H)$ (**3**), which is observed as an unstable intermediate by ^1H NMR. Compound **3** decomposes in solution ($t_{1/2} < 30$ min at 25 °C) with elimination of $SiMe_4$, presumably via the reactive intermediate $Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)$. However, generation of this 16e$^-$ intermediate in the presence of trimethylphosphine as a trapping ligand yields the stable η^2-silanimine complex $Cp_2Zr(\eta^2\text{-}SiMe_2{=}N^tBu)(PMe_3)$ (**4**, 73% isolated).

As depicted in Scheme I, and in analogy to metal–olefin complexes, the bonding of the silanimine fragment to the metal is expected to fall between the two extreme resonance forms of a metallacycle (sp^3 hybridization at Si) and a π-donor complex (sp^2 hybridization at Si). The molecular structure of **4** as determined by a single-crystal X-ray diffraction study is shown in Figure 1.[9]

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(8) Full details on the preparation and characterization of new compounds are included in the supplementary material.

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