These spectra demonstrate the feasibility of ultraviolet resonance Raman spectroscopy in the far ultraviolet region with use of existing commercial laser sources. They also demonstrate the utility of this technique for observation of highly excited vibrational levels of a small yet interesting molecule.

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Carbon-13 CIDNP Investigation of the Thermal Decomposition of *tert*-Butyl Phenylperacetate[1]

John Kurhanewicz and George R. Jurch, Jr.*

Department of Chemistry, University of South Florida
Tampa, Florida 33620

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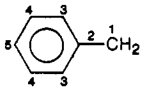
The initial work of Bartlett and Hiatt[2] led the authors to postulate two mechanisms for the thermal decomposition of *tert*-butyl peresters, $R{-}C(O){-}O{-}O(CH_3)_3$: a one bond O–O cleavage (nonconcerted) when R was not a stable alkyl radical and a concerted O–O and R–C bond cleavage when R was a stable radical. Subsequent kinetic work involving: substituent effects,[3] cage effects,[4] stereochemical effects,[5] secondary deuterium isotope effects,[6] and activation volumes,[7] viscosity dependence,[8] ring strain effects,[9] and isotopic labeling[10] raised some serious questions about the twofold nature of the thermal decomposition but even revised versions still contained the two pathways. An initial proton CIDNP investigation of the thermal decomposition of *tert*-butyl phenylperacetate (I) indicated a number of net polarizations which arose from sorting encounters between triplet radical pairs[11] and agreed with earlier unpublished proton CIDNP results obtained for *tert*-butyl perpivalate.[12]

In this work we will describe carbon-13 polarizations obtained during the thermal decomposition of labeled (I)[13] in hexachloroacetone and cyclohexanone.[14] The polarizations are listed in Table I. All polarizations were assigned based on the addition of known compounds to the decomposed sample and GC-mass spectral analysis of the decomposed sample.[15] Individual carbon assignments were aided by multiplicity determinations by using NOE, SEFT, or INEPT II multiplicity analysis.

Table I. CIDNP Polarizations during the Thermal Decomposition of Labeled[a] *tert*-Butyl Phenylperacetate in Hexachloroacetone and Cyclohexanone

compd	carbon[b]	chem shift (ppm)	polarztn obsd	net equation			
				μ	ϵ	Δ_g	a_i
Polarizations in Hexachloroacetone							
bibenzyl	C-2	141.8	E	+	–	–	–
cis-stilbene	C-1	124.4	A	+	–	–	+
	C-2	131.5	E	+	–	–	–
benzyl phenyl acetate	carbonyl	170.2	E	+	+	+	–
carbon dioxide		124.2	E	+	+	+	–
benzyl chloride	C-1	45.6	A	+	–	–	+
	C-2	137.5	E	+	–	–	–
	C-3	128.3	A	+	–	–	+
hexachloroethane		107.1	E	+	–	+	+
1,1-dichlorostyrene	C-1	121.3	A	+	+	+	+
	C-2	128.0	E	+	+	–	+
	C-3	135.2	A	+	+	–	–
benzyl pentachloroacetone	carbonyl	180.4	E	+	+	+	–
	CCl	83.4	A	+	+	+	+
	C-1	51.9	E	+	+	–	+
	C-2	135.2	A	+	+	–	–
Polarizations in Cyclohexanone							
benzyl *tert*-butyl ether	C-2	140.61	A	+	+	–	–
	C-3	128.80	E	+	+	–	+
bibenzyl	C-1	37.22	A	+	–	–	+
	C-2	141.76	E	+	–	–	–
	C-3	128.41	A	+	–	–	+
benzyl phenyl acetate	carbonyl	171.60	E	+	+	+	–
carbon dioxide		124.31	E	+	+	+	–
toluene	C-1	20.56	E	+	–	+	+
	C-2	138.12	A	+	–	+	–
α-benzylcyclohexanone	carbonyl	209.19	E	+	+	+	–
	C-α	51.89	A	+	+	+	+
	C-1	33.52	E	+	+	–	+
	C-2	144.51	A	+	+	–	–

[a] Carbon-13 labeled carbonyl. [b] Compounds are numbered in the following way



By using the qualitative CIDNP rules of Kaptein[16] and the experimental net polarizations, the signs of the product factor, ϵ, and multiplicity, μ, were deduced by examining all the possible reaction pathways. These results are presented in Table I and indicate all the steps leading to polarization involve triplet radical pairs. This can be explained by a phenomenon initially coined "radical pair substitution", by den Hollander and Kaptein.[17,18]

A mechanism that can account for all the CIDNP and kinetic data is shown in Scheme I. The proposed mechanism involves nonconcerted cleavage to form a singlet *tert*-butyloxy–phenylacetyloxy radical pair. Spin correlation is lost due to the *tert*-butoxy radical, as indicated by the earlier proton CIDNP stud-

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(13) This perester was prepared by the reaction of C-13 carbonyl labeled phenylacetic acid with thionyl chloride and then the subsequent reaction of the acid chloride with *tert*-butyl hydroperoxide according to the procedure of Bartlett and Hiatt:[2] IR (neat) 3075–3025 (aromatic C–H), 2956–2988 (aliphatic C–H), 1776 (carbonyl), 1605–1450 (aromatic C=C), 1195 (C–O), 850 (O–O), 705 (5 adjacent hydrogens) cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.23 (s, 9 H), 3.58 (s, 2 H), 7.26 (s, 5 H) ppm; ^{13}C NMR ($CDCl_3$) 25.74 (q, 3 C), 38.26 (t, 1 C), 83.28 (s, 1 C), 127.10 (d, 1 C), 128.40 (d, 2 C), 128.89 (d, 2 C), 132.68 (s, 1 C), 168.33 (s, 1 C) ppm.

(14) Labeled *tert*-butyl phenylperacetate was decomposed inside the probe of a Joel FX90Q at temperatures ranging from 70 to 135 °C by using deuteriated Me_2SO as a lock.

(15) The GC-MS product studies were carried out on a Hewlett Packard 5890A GC with a 59700 series mass selective detector by using a 2 M capillary carbowax column with a 0.20 mm diameter (HP 298-12-09-B). The product mixture was diluted (100/1) with methanol and the GC run temperature programmed from 70 to 240 °C.

(16) Kaptein, R. *J. Chem. Soc.* D **1971**, 732. The net equation consists of four terms ($T_N = \mu\epsilon\Delta g a_i$); μ refers to the multiplicity of the radical pair at the time of its formation, ϵ is evaluated from the type of product-forming reaction, Δg is the difference in spectroscopic splitting factors of the radical pair, and a_i is the sign of the hyperfine coupling constant.

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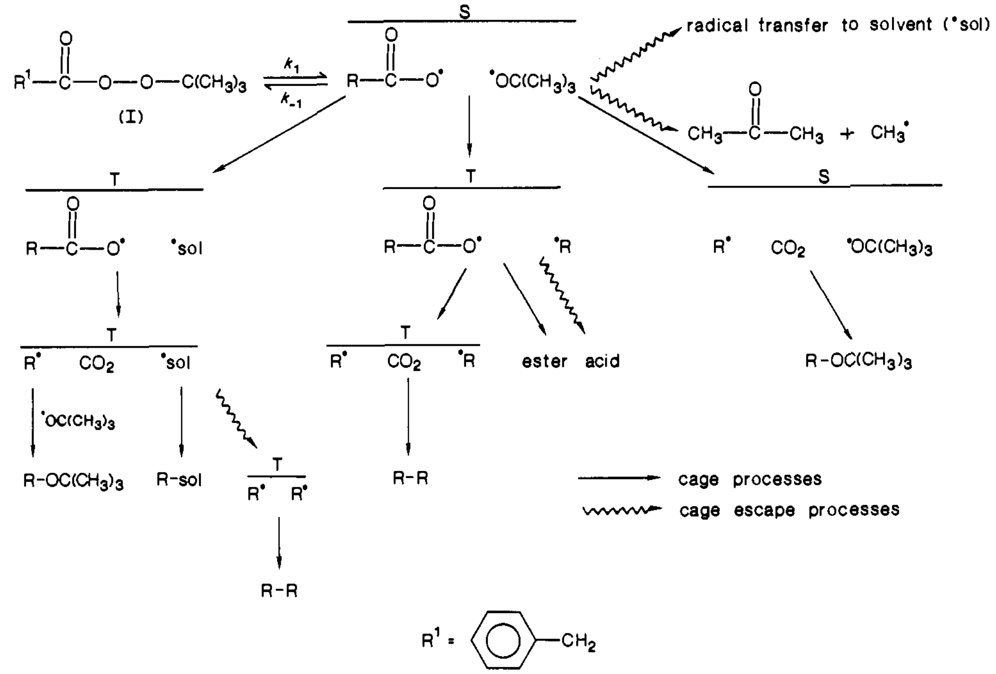
Scheme I



ies[11,17] and further supported by the C-13 CIDNP data. Since the *tert*-butyloxy radical cannot act as a radical pair partner, secondary triplet pairs form consisting of acyloxy–benzyl and acyloxy–solvent radical pairs. The acyloxy–benzyl triplet pair combine to a very small extent before decarboxylation. Evidence for this acyloxy intermediate in our CIDNP studies consists of the emissive polarizations of carbon dioxide and the C-13 labeled benzyl phenylacetate. The existence of the acyloxy radical as an intermediate has been corroborated by the recent work of Falvey and Schuster[19] and Lloyd and Williams.[20] The polarized bibenzyl arises from coupling after decarboxylation within the acyloxy–benzyl solvent cage or from escape from the acyloxy-solvent derived radial cage. The polarization observed for *cis*-stilbene is an example of a "memory effect",[18] with "spin sorting" occurring in the same step as in the bibenzyl case. Decarboxylation of the phenylacetyloxy radical in the initial singlet pair, with subsequent ether production, would not lead to polarization due to the inability of the *tert*-butoxy radical to act as a spin sorting partner. In hexachloroacetone the ether is formed in substantial amounts but shows no polarization, yet in cyclohexanone the C-2 and C-3 aromatic carbons show a strong enhanced absorption and emission, respectively. Knowing the signs of all other terms of the net equation, the phase of the polarizations indicate that the radical precursors leading to ether product had triplet multiplicity. The explanation for this is that in cyclohexanone the benzyl radical has a long enough lifetime that it attains concentrations high enough to scavenge *tert*-butoxy radicals which escape β-scission and reaction with solvent. This is an example of a scavenging process which is competitive with geminate recombination;[21] therefore, ether is produced by two pathways: within the primary cage which shows no polarization and in the bulk solution which leads to a polarized product. Evidence that solvent-derived radicals are involved in geminate pairs are the polarizations observed for benzyl chloride, benzyl pentachloroacetone, hexachloroethane, 1,1-dichlorostyrene,[22,23] toluene, and α-benzylcyclohexanone. Product studies also indicate that approximately 10% of the HCA is consumed during the decomposition.

Therefore, these CIDNP results indicate that *tert*-butyl phenylperacetate decomposes by a nonconcerted pathway with the observed rate of decomposition being dependent on the strength of the O–O bond, the rate of decarboxylation, and the rate of internal return.

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Vibrational Spectroscopic Characterization of the CCO Ligand and the Possible Occurrence of CCO on Surfaces

Michael J. Sailor and Duward F. Shriver*

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

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As outlined below there is abundant evidence from metal cluster chemistry that a carbon atom capping a three-metal array has a high affinity for CO, leading to the formation of CCO. Accordingly, we propose that CCO may exist on a carbided closest-packed metal surface in the presence of CO. For example, the surface carbide species on a Fischer–Tropsch catalyst[1-3] may be present as CCO. Vibrational spectroscopy represents one of the most promising methods for detecting CCO, and, therefore, we have undertaken vibrational characterization of CCO in the structurally characterized cluster $[Ru_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}CCO)]^{2-}$, **1**.

One striking example of the propensity of a capping C atom to couple with CO is the abstraction of halogen from a capping CX ligand to produce a capping CCO, eq 1.[4,5] Another example

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