tained T_1 values from partially relaxed spectra of the denatured protein (Table I). The correlation times of the α-carbons are much shorter than in the native protein (Table I), indicating an appreciable degree of segmental motion in the backbone of denatured ribonuclease. Significantly, τ_R of the ϵ-carbons of the lysine residues is not measurably affected by denaturation.

It is apparent that PRFT nmr spectra provide a powerful technique for studying proteins in solution. In the past, the most common way of using magnetic resonance to study biopolymer reorientation in solution has been by means of artificially attached electron[13] or nuclear spin labels.[14] Partially relaxed carbon-13 Fourier transform nmr is an alternative technique which provides a *multitude* of built-in probes in any *unmodified* biopolymer.

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(15) National Institutes of Health Predoctoral Fellow, 1967–1970.

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Chemically Induced Dynamic Nuclear Polarization in Products from Radical Displacement Reactions

Sir:

Although it is generally accepted that chemically induced dynamic nuclear polarization (CIDNP) is only observed in the nmr spectra of molecules which have recently been formed from free radical precursors, our picture of the nature of the polarization process is still incomplete. The most convincing treatments have been those of Kaptein and Oosterhoff[1] and Closs,[2,3] which assume that nuclear polarization is a consequence of electron spin polarization accompanying the interaction of radical pairs within a solvent cage, and apply directly only to bimolecular radical processes of coupling and disproportionation.

A few cases of polarized spectra of products of radical displacement reactions have also been reported,[4] but here the details of the polarization process are obscure. We now report results with several displacement reactions involving benzyl radicals, where we believe for the first time both the displacement step and the reaction conditions have been systematically varied. We find significant changes in the polarized spectra observed, and propose an explanation.

When phenylacetyl peroxide is decomposed at 40° in CCl_4 containing CCl_3Br, the products shown in Table I are obtained. All but benzyl bromide (A) arising from the displacement process (eq 1) and the

$$C_6H_5CH_2\cdot + CCl_3Br \longrightarrow C_6H_5CH_2Br + CCl_3\cdot \qquad (1)$$

$C_6H_5CH_2CCl_3$ (B) and C_2Cl_6 (from radical coupling) are presumably products of cage recombination of initial radical or ion pairs.[5] Benzyl radicals are effectively trapped *via* eq 1 or by combination with $CCl_3\cdot$

$$C_6H_5CH_2\cdot + \cdot CCl_3 \longrightarrow C_6H_5CH_2CCl_3 \qquad (2)$$

radicals since yields of bibenzyl do not rise until the CCl_3Br concentration is reduced below 0.1 *M*.[6]

Table I. Products from the Decomposition of Phenylacetyl Peroxide in CCl_4–CCl_3Br[a]

Product	δ_{TMS}, ppm[b]	% yield
$(PhC\mathit{H}_2)_2$	2.87	20–23
$PhC\mathit{H}_2COO$- $C\mathit{H}_2Ph$	3.55 5.04	12–20
$PhC\mathit{H}_2COO$- $COOC\mathit{H}_2Ph$	3.64 5.15	23–28
$PhC\mathit{H}_2CCl_3$	3.87	3–9
$PhC\mathit{H}_2Br$	4.38	15–27
Other benzyl deriv	4.56, 5.24, 5.28	6–7

[a] ~0.1 *M* peroxide, 0.1–3 *M* CCl_3Br, 40°. [b] Nmr peaks of *underlined* hydrogens. Analyses based on relative integrated intensities.

When the decompositions are carried out at 40° in the spectrometer we observe strongly polarized spectra of the benzyl hydrogens of both benzyl bromide (emission, δ = 4.38) and $C_6H_5CH_2CCl_3$ (absorption, δ = 3.87). We find no polarization of any cage products in this system.[7] The time dependence of spectral intensity is shown in Figure 1, together with that of bibenzyl which monitors the peroxide decomposition rate. The actual enhancement factor α/β for the polarization may be calculated for the data of Figure 1 *via* the relation

$$(I_\infty - I)/I_\infty = (1 - \alpha k_1/\beta k_2)([P]/[P]_0) \qquad (3)$$

where I and I_∞ are the integrated line intensities[8] at some point during reaction and at the end of reaction when all relaxation processes are complete, [P] is peroxide concentration, $k_1 = k_d$ for peroxide decomposition, k_2 is the rate constant for spin relaxation of the transition giving rise to the line, and α/β is a ratio of numbers proportional to the molar absorbances of polarized and unpolarized species (for emission, α is

(1) R. Kaptein and J. L. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969).

(2) G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969).

(3) G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2183, 2186 (1970).

(4) (a) J. Bargon and H. Fischer, *Z. Naturforsch. A*, **22**, 1556 (1967); *ibid.*, *A*, **23**, 2109 (1968); (b) R. Kaptein, *Chem. Phys. Lett.*, **2**, 261 (1968); (c) H. R. Ward, R. G. Lawler, and R. A. Cooper, *Tetrahedron Lett.*, 527 (1969); (d) S. V. Rykov, A. L. Buchachenko, and A. V. Kessenich, *Spectrosc. Lett.*, **3**, 55 (1970), and references therein; (e) T. Koenig and W. R. Mabey, *J. Amer. Chem. Soc.*, **92**, 3804 (1970).

(5) Phenylacetyl peroxide decomposes rapidly by concerted multibond scission: P. D. Bartlett and J. E. Leffler, *ibid.*, **72**, 3030 (1950). We have recently suggested that both "polar" and "radical" cage products in such systems are formed subsequent to a single rate-determining transition state: C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiaonnou, *ibid.*, **92**, 4927 (1970).

(6) In CCl_4 alone, the bibenzyl yield is 43%, less than 1% benzyl chloride is formed, and cage products are unchanged.

(7) Polarization is also observed in the aromatic hydrogen region but cannot be resolved in detail.

(8) Use of integrated intensities is important, since our polarized spectra have abnormally narrow line widths ($\nu_{1/2}$ 0.6 cps) compared with the unpolarized species (1.1 cps).

negative). The derivation of eq 3 will be given elsewhere, but simply assumes that polarized benzyl bromide is formed at a rate proportional to peroxide decomposition and relaxes with a rate constant k_2.[9] In Figure 1, $k_1 = 4 \times 10^{-3}$ sec^{-1}, $k_2 = 1 \times 10^{-1}$ (our measurements), and $\alpha/\beta = -27$, for benzyl bromide.

Similar polarizations are observed in the spectra of benzyl chloride obtained under comparable conditions in the presence of either CCl_3SO_2Cl or *tert*-butyl hypochlorite (together with B in the first case), benzyl iodide, and B in the presence of CCl_3I (except that emission and absorption are now reversed!), and of toluene in the presence of thiophenol or *tert*-butyl mercaptan. The bibenzyl monitor shows that peroxide decomposition rates are similar in all these systems, so that induced decompositions are unimportant.

On the other hand, enhancement factors in the CCl_3Br system are sensitive to both peroxide and CCl_3Br concentration. Further, benzyl bromide produced in the short-chain bromination of toluene by CCl_3Br using *tert*-butyl hyponitrite initiator (5%) is only weakly polarized[10] and benzyl chloride from toluene-*tert*-butyl hypochlorite shows no polarization whatever. Neither was polarization noted in the small amount of benzyl chloride obtained on decomposing phenylacetyl peroxide alone in CCl_4.

Our results show plainly that *the same displacement reaction may give varying yields of polarized species depending upon reaction conditions.*[11] This clearly rules out any mechanism of polarization during the displacement step as has been suggested by Gerhart and Osterman.[12] Since polarization is sensitive to peroxide concentration and polarized products are observed which are not derived from radicals initially produced in pairs (*e.g.*, benzyl bromide and $CHCl_3$ from the CCl_3Br–toluene reaction), a second alternative, *polarization during separation of initial radical pairs, is also eliminated.*[13] The above results, together with the general finding that polarization decreases in chain processes where a low radical concentration still gives rise to reasonable product yields, suggest that the critical variable in our systems is essentially the *total radical flux* and accordingly that *polarization occurs from subsequent near encounters of radical pairs*, which, in any system, maintains a quasi-steady-state concentration of polarized species.[14] *If a thus polarized radical undergoes a displacement (or other) reaction prior to relaxation, polarized products result.*[15] As a consequence, enhancement factors depend upon both radical flux and the relative rates of radical reactions and radical relaxations.

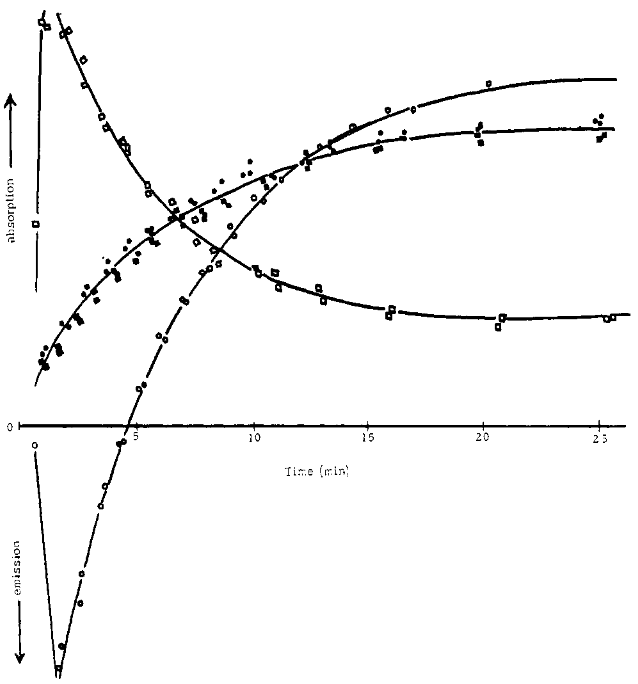

Figure 1. Integrated pmr methylene peak intensity variation with time for $C_6H_5CH_2CH_2C_6H_5$ (■, ●), $C_6H_5CH_2Br$ (○), and $C_6H_5CH_2CCl_3$ (□) from two reactions of 0.11 *M* phenylacetyl peroxide and 0.32 *M* bromotrichloromethane in carbon tetrachloride at 40°.

We have carried out a detailed kinetic analysis of this model which proves to be consistent with our data and yields plausible rate constants for both the polarizing near-approach ($k \sim 10^{10}$ l./mol sec) and subsequent relaxation of the polarized radicals ($k \sim 10^4$ sec^{-1}) and contains no other adjustable parameters. We believe that this is the first direct experimental measurement of a rate constant for the polarization process and details will be reported in our full paper.

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(9) A similar treatment has been given by T. Koenig and W. R. Mabey.[4e]

(10) A strong emission from $CHCl_3$ is also observed. Polarized spectra from $CHCl_3$ are particularly intense due to its slow relaxation.[4e]

(11) The important distinction must be made between the *formation* of polarized species and the actual *observation* of polarized spectra, since the latter depends as well upon the relative rates of radical formation and relaxation of nucleon spins (*cf.* eq 3). However overall half-lives of all reactions reported here were at least as short as the peroxide decompositions.

(12) F. Gerhart and G. Osterman, *Tetrahedron Lett.*, 4705 (1969).

(13) This need not always be the case, and a system involving a displacement reaction in which polarization occurs by this mechanism has recently been reported by G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, 92, 7227 (1970). We thank the authors for a copy of their manuscript prior to publication.

(14) If current theories[1,2] are correct these near encounters must be sorting processes in which lone pairs react and others separate. Indeed, our finding of opposite signs of polarization for displacement and coupling products give further support to this interpretation.

(15) We assume that effective benzyl radical polarization requires interaction with unlike radicals, in most of our cases, with $CCl_3\cdot$. Thus in the phenylacetyl peroxide–carbon tetrachloride system the very low reactivity of CCl_4 with benzyl radicals leads to formation of very few $CCl_3\cdot$ radicals and, accordingly, no polarization of the benzyl chloride.

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Singlet Ground State in Tetrabutylammonium Bis(toluene-3,4-dithiolato)cobaltate

Sir:

At high temperatures (77–300°K), tetrabutylammonium bis(toluene-3,4-dithiolato)cobaltate, (n-Bu_4N)[Co(tdt)$_2$], exhibits a magnetic moment of 3.18 BM.[1] Also, measurements on solutions of the compound in various solvents, including pyridine, at room temperature yield moments of 3.33–3.43 BM.[1] From these observations, it was logically concluded that this compound was

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(1) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Amer. Chem. Soc.*, 88, 43 (1966).