

If decay from a common twisted state is involved in the sensitized and unsensitized experiments, the photostationary state derived from direct irradiation should be related to that obtained with high-energy sensitizers in the following way

$$\frac{[\text{syn}]_s}{[\text{anti}]_s} = \frac{\epsilon_{\text{anti}} [\Phi_{\text{anti} \rightarrow \text{syn}}]}{\epsilon_{\text{syn}} [\Phi_{\text{syn} \rightarrow \text{anti}}]}$$

This relationship predicts a sensitized photostationary state of syn/anti = 2.36 ± 0.3 for acetophenone, 2.04 ± 0.2 for *p*-methoxyacetophenone, and 2.21 ± 0.2 for propiophenone. The calculated photostationary state values are greater than the observed values by a factor of ca. 1.4.³¹

The difference between the two numbers is an indication that crossing to triplets is not the sole fate of excited singlets, although the closeness of the values may indicate that the isomerization induced by direct irradiation is passing, in part, through the triplet.^{31a} The finding of lower than predicted sensitized photostationary state values may also indicate that the identity of the intersystem crossing terms may not be the same for both isomers. Since the sum of the quantum yields, $\Phi_{\text{syn} \rightarrow \text{anti}} + \Phi_{\text{anti} \rightarrow \text{syn}}$, is less than unity it would appear that deactivation of singlet and/or triplet states of the oxime ethers includes radiationless decay processes³² which proceed by paths not involving syn-anti isomerization. The source of inefficiency may be related to energy-degrading processes within a twisted excited state or may possibly involve relaxation of planar excited states in competition with decay of the twisted form. The inefficiency encountered with the sensitized experiments may indicate that not all acetophenone triplets are effective in generating a twisted imine triplet. Although radiationless paths which maintain geometric integrity are important to a degree, syn-anti isomerization provides the major route for deactivation of the excited imine state.

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(30) The fact that the $\Phi_{\text{anti} \rightarrow \text{syn}}$ is slightly dependent on syn oxime concentration is also compatible with a lower than diffusion-controlled quenching rate for the syn isomer.

(31) Similar discrepancies have been observed by deMayo and co-workers in the photoisomerization of benzaldoxime: H. Izawa, P. deMayo, and T. Tabata, *Can. J. Chem.*, **47**, 51 (1969).

(31a) NOTE ADDED IN PROOF. These results are also consistent with a pathway that involves only excited singlets in the direct irradiation. This point will be discussed in greater detail in our full publication.

(32) Although no phosphorescence or fluorescence emission was observed from either isomer, these isomers did quench the phosphorescence emission of acetophenone ($E_T = 73.6$), benzophenone ($E_T = 68.6$), and phenanthrene ($E_T = 62$). The sensitization and phosphorescence studies confirm the fact that triplet energy occurs, and that transfer is possible even when the triplet energy of the sensitizer is insufficient to promote the oxime ether (1 or 2) to its spectroscopic triplet state.

(33) Alfred P. Sloan Foundation Fellow, 1968-1972.

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Effect of Nuclear Spin Relaxation on Intensity Patterns of Multiplet Spectra in Chemically Induced Dynamic Nuclear Polarization¹

Sir:

Chemically induced dynamic nuclear polarization has been successfully explained in terms of nuclear spin state dependent triplet singlet intersystem crossing in correlated radical pairs.² According to this theory, the population N_n of the n th nuclear spin state of a product in a reacting system is given by eq 1, where

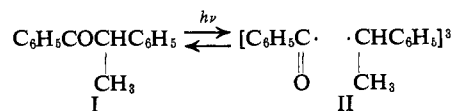
$$\frac{d}{dt} N_n = k_r [{}^m M] W_n + \sum_i (w_{i \rightarrow n} N_i - w_{n \rightarrow i} N_n) \quad (1)$$

$k_r [{}^m M]$ is the rate of radical pair formation from the precursor molecule M with multiplicity m and W_n is the nuclear spin state dependent probability of product formation from the pair. The $w_{i \rightarrow n}$ and $w_{n \rightarrow i}$ are the transition probabilities per unit time for the upward and downward relaxation processes connecting the nuclear spin levels i with level n . Neglecting the small nuclear Zeeman energy differences, we obtain eq 2 for the nmr

$$\begin{aligned} \frac{d}{dt} \text{Int}_{nm} &\propto \frac{d}{dt} (N_n - N_m) = k_r [{}^m M] (W_n - W_m) - \\ &2w_{mn}(N_n - N_m) + \sum_{i \neq m} w_{in}(N_i - N_n) - \sum_{i \neq n} w_{im}(N_i - N_m) \end{aligned} \quad (2)$$

line intensity Int_{nm} with $w_{in} = w_{i \rightarrow n} = w_{n \rightarrow i}$. In all previous treatments it has been assumed that only the first term in eq 2 contributes to the relative intensities of CIDNP spectra. However, independent of the relaxation mechanism assumed, the last two relaxation terms in eq 2 never vanish for multilevel systems. *Therefore, relative line intensities in CIDNP multiplet spectra are only in part determined by the rates of product formation from the radical pair. Nuclear spin relaxation in the final product may play an important part.*³

Strong evidence for this fact is provided by the photo-induced α cleavage of phenyl α -phenylethyl ketone (I) to form the radical pair II.⁴ Re-formation of I from



correlated radical pairs ("cage" recombination) occurs with strong emission of the benzylic methine proton quartet with line 1 (low-field line) missing (Figure 1b). Considering only the first term in eq 2, this fact leads to a g factor difference in II of $\Delta g = 3.6 \times 10^{-3}$.⁵ It is important to note that this conclusion is independent

(1) Supported by National Science Foundation Grant No. 18719X.

(2) (a) G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969); (b) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969); (c) H. Fischer, *Z. Naturforsch. A*, **25**, 1951 (1970); (d) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 7227 (1970); (e) F. J. Adrian, *J. Chem. Phys.*, **54**, 3912 (1971); (f) R. Kaptein, Ph.D. Thesis, Leiden, 1971; (g) G. L. Closs, *Spec. Lect. XXIIIrd Int. Congr. Pure Appl. Chem.*, **4**, 19 (1971).

(3) The possible importance of relaxation effects in changing relative multiplet line intensities has recently been pointed out: M. Lehnig and H. Fischer, *Z. Naturforsch. A*, **25**, 1963 (1970); R. Kaptein, see ref 1f, p 53.

(4) The triplet multiplicity of the reacting state was verified by effective quenching of the reaction with piperylene.

(5) Calculated with $|a_\alpha| = |a_\beta| \approx 17$ G for the hyperfine coupling constants in the α -phenylethyl radical; see D. W. Skelly, R. G. Hayes and W. H. Hamill, *J. Chem. Phys.*, **43**, 2795 (1965).

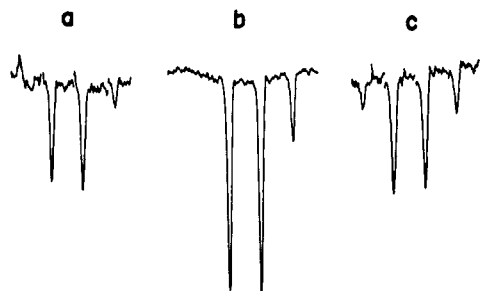


Figure 1. The polarized quartet of the benzylic methine proton in I in (a) presteady-state (by scanning through each quartet line immediately after ($\Delta t \approx 3$ sec) starting the light reaction), (b) steady-state, and (c) poststeady-state condition (by scanning through each quartet line immediately after ($\Delta t \approx 3$ sec) stopping the light reaction).

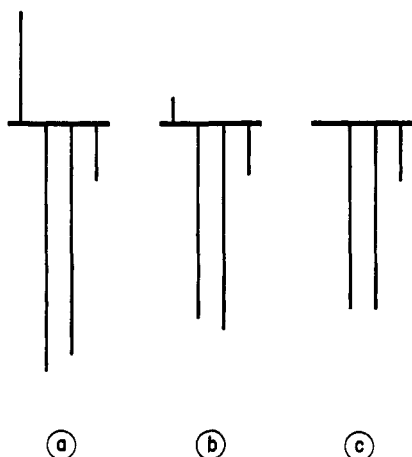


Figure 2. The calculated⁶ steady-state quartet of the methine proton in I, using W_n from ref 2e, (a) with neglect of relaxation, (b) inclusion of intermolecular spin lattice relaxation, $Q = 1$ and $P = 0$,⁶ and (c) additional inclusion of nuclear dipole-dipole coupling within the methyl group (with $Q = 1$, the amount of intramolecular dipolar coupling, P , necessary to cancel line 1, increases the summed probabilities of the transitions $m_z = \pm 1/2 \rightarrow \pm 1/2$ and $m_z = \pm 1/2 \rightarrow \mp 1/2$ within the A_3 level manifolds by 14 and 18%, respectively).

of the various analytical forms of W_n^{2a-g} and is also not changed if allowance is made for the small contributions of the phenyl protons in II. However, a careful determination of Δg by esr yields a value of $(2.0 \pm 0.2) \times 10^{-3}$ which, on the basis of only the first term in eq 2, leads to a predicted quartet with line 1 in strong absorption (Figure 2a). The discrepancy between the calculated and the experimental spectra is due to the neglect of the relaxation terms in eq 2.

To illustrate this point we first consider only intermolecular spin lattice relaxation processes, using the transition probabilities calculated⁶ for an A_3X spin

(6) The calculations are based on Redfield's density matrix theory. For the relaxations induced by intramolecular dipolar coupling within the methyl group, the simplest model has been adopted (P. S. Hubbard, *Phys. Rev.*, **109**, 1153 (1958); **111**, 1746 (1958)) in which additional relaxations due to internal rotation of the methyl group are neglected (see, e.g., P. S. Hubbard, *J. Chem. Phys.*, **52**, 563 (1970)). The equivalent of eq 2 is conveniently written in the form

$$\frac{d}{dt}(\text{Int}) \propto \frac{d}{dt}(\Delta N) = (\Delta P) + w[(R)_{X^{\text{inter}}} + Q(R)_{A^{\text{inter}}} + QP(R)_{A^{\text{intra}}}] \cdot (\Delta N)$$

where the vector (ΔN) contains all the population differences $\Delta N_{nm} = N_n - N_m$, (ΔP) is the CIDNP vector corresponding to the first term in eq 2, and (R) 's are the corresponding inter- and intramolecular relaxation matrices of protons A and X, respectively. In (R) , cross-correlation terms have been taken into account for the steady-state calculations (Figure 2b, c). Q and P are adjustable parameters which allow us to

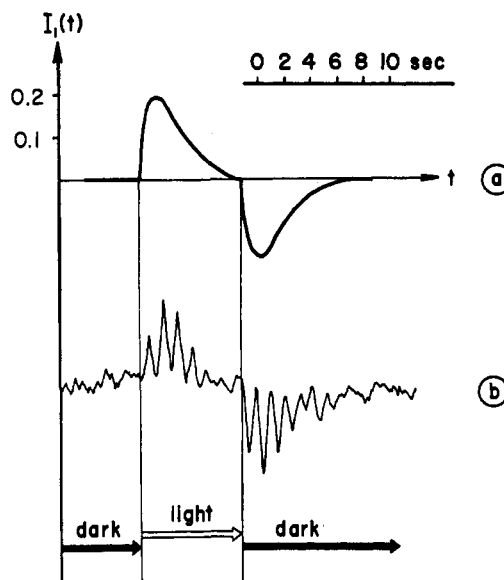


Figure 3. The calculated (a)⁶ and experimental (b) transient intensities of line 1 of the methine quartet in I. The ordinate scale in diagram 3a is given in fractions of the intensity of line 1 calculated with $Q = 0$.

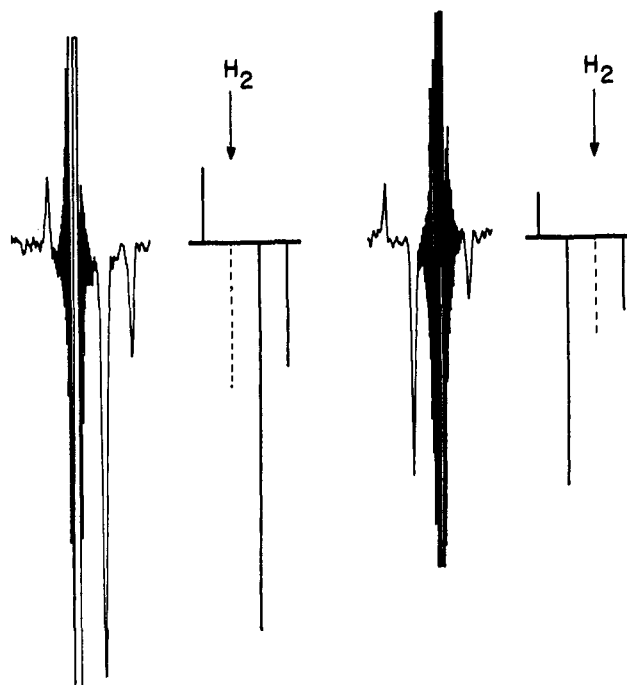


Figure 4. The polarized methine quartet of I, using a second resonance field to irradiate lines 2 and 3 selectively ($H_2 \approx 0.1$ mG). The stick diagrams are calculated according to footnote 6 with an additional rf induced transition probability, $w_{rf} = 5w$, included in $(R)_{X^{\text{inter}}}$.

system interacting with a randomly fluctuating lattice field. The set of steady state conditions $d(N_n - N_m)/dt = 0$ is then easily solved. The result shows (Figure 2b) that, even if we assume all nuclear spins to be equally coupled to the lattice, there is a substantial effect on the appearance of the spectrum caused by the fact that

vary the relative coupling of A and X to the lattice and to change the fraction of intramolecular relaxation. They are chosen to give the best fit between the calculated and experimental steady-state spectra (see footnote a of Figure 2). The errors induced by neglect of cross-correlation terms can be compensated for satisfactorily by readjusting Q and P . This method leads to a considerable reduction of the relaxation problem and was adopted for the further calculations (Figures 3 and 4).

each line borrows intensity from all the other multiplet lines, the mixing effect between adjacent lines being dominant. It is possible to allow for different rate constants of relaxation transitions involving different nuclei, but the general result is the same. An important special case is the inclusion of relaxation transitions induced by intramolecular nuclear dipole-dipole coupling. Since this interaction is strongly dependent on the distance between two protons ($\propto 1/r^3$), we may consider only the effects of dipolar coupling within the methyl group.⁶ Such a coupling increases the mixing effects of the X quartet line intensities and especially reinforces the borrowing of intensity from second next nearest neighbor lines. As shown in Figure 2b, inclusion of intermolecular spin lattice relaxation cuts the intensity of line 1 to about one quarter of its original intensity. Additional inclusion of dipolar coupling within the methyl group cancels line 1 completely (Figure 2c).

It has long been recognized that the *absolute* intensities of CIDNP spectra are directly proportional to the nuclear relaxation times.⁷ Detailed consideration of eq 2 leads to the interesting prediction that the *relative* intensities of multiplet lines in CIDNP should change during the course of the reaction. At the beginning of the reaction, the line intensities are dominated by the first term in eq 2 because relaxation is less important at reaction times short compared to the nuclear relaxation times. This presteady state has a counterpart in the poststeady-state period, after the reaction has been stopped, where the intensities are governed by the relaxation terms in eq 2. The experimental pre- and poststeady-state spectra are shown in Figure 1 (a and c). As predicted, the presteady-state spectrum approaches the one calculated with neglect of relaxation (Figure 2a), with line 1 in absorption. Accordingly, the poststeady-state spectrum shows the same line in emission. The transient intensity of line 1, obtained by recording line 1 repeatedly for a time interval at the beginning and end of the reaction (Figure 3b), demonstrates the mirror-image relationship between the pre- and poststeady-state behavior and shows a striking similarity to the calculated envelopes of Figure 3a.

To demonstrate further the important role of nuclear spin relaxation in CIDNP, the methine quartet was recorded while one of the quartet lines was simultaneously irradiated with moderate rf power so as to diminish considerably the population difference of that line without significant perturbation of the nuclear spin levels.⁸ Effective reduction of the strong emission of line 2 or 3 should then lead to absorption for line 1, as indicated by the calculated stick diagrams (Figure 4). Again, these predictions are nicely supported by the experimental spectra shown in Figure 4.

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(7) (a) R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5519 (1967); (b) G. L. Closs and L. E. Closs, *ibid.*, **91**, 4549 (1969).

(8) B. D. Nageswara Rao, *Advan. Magn. Resonance*, **4**, 271, 286 (1970).

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Stripping Reactions of Gaseous Ions in the Mass Spectrometer

Sir:

We describe a new reaction in gaseous polyatomic ions, some aspects of its mechanism, and its role in generating a new type of mass spectrum of potential analytical value.

We have previously utilized charge-transfer reactions of the type $m^{2+} + N \rightarrow m^+ + N^+$ (where m^{2+} is any doubly charged ion and N any neutral gas or vapor) to separate singly and doubly charged ions in the mass spectrometer and so to obtain pure doubly charged ion spectra.¹ The reverse reaction, leading to an increase in the number of charges borne by the ion, has apparently only been studied for high energy (>10 keV) atomic ions.² We now report that the process $m^+ + N \rightarrow m^{2+} + N + e^-$ occurs with facility when polyatomic singly charged ions of 5–10-keV energy impinge upon a variety of collision gases. Moreover, if the collection of singly charged ions formed from a typical organic compound in the ion source of the mass spectrometer is passed through a field-free collision region (pressure of neutral 10^{-6} – 10^{-4} Torr), the resulting doubly charged ions can be separated from singly charged ions by operating the electric sector at half the normal value (E) and then mass analyzed to give a new type of mass spectrum (the $E/2$ mass spectrum). The aniline $E/2$ mass spectrum³ appears in Figure 1; it is juxtaposed against the normal singly charged ion mass spectrum (electric sector value E , ion accelerating voltage V) and the doubly charged ion mass spectrum obtained by charge exchange (electric sector value $2E$). The three spectra are markedly different and experiments are underway to exploit the analytical possibilities of the new type of spectrum by attempting to distinguish isomers which give identical singly and doubly charged ion mass spectra.

It is important to note that with the electric sector set at $E/2$, ions undergoing the reaction $m^+ \rightarrow m^+/2 + m/2$, either collision induced or unimolecular, will be passed. In the aniline case the unimolecular $m^+ \rightarrow m^+/2 + m/2$ process did not give a detectable signal at low collision gas pressures ($\sim 1 \times 10^{-7}$ Torr). Fortunately the collision-induced component of this fragmentation could easily be distinguished from the charge-stripping process using two observations: (i) the charge-stripping process yields maximum signal if the sector voltage is decreased slightly from exactly $E/2$ or if the accelerating voltage is increased to slightly more than V ; (ii) peaks due to the collision-induced fragmentation are much broader than those due to the

(1) (a) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Org. Mass Spectrom.*, **3**, 455 (1970); (b) J. H. Beynon, A. Mathias, and A. E. Williams, *ibid.*, **5**, 303 (1971); (c) T. Ast, J. H. Beynon, and R. G. Cooks, *J. Amer. Chem. Soc.*, in press; (d) T. Ast, J. H. Beynon, and R. G. Cooks, *Org. Mass Spectrom.*, in press.

(2) (a) H. Ewald and W. Seibt, "Recent Developments in Mass Spectrometry," K. Ogata and T. Hayakawa, Ed., University Park Press, Baltimore, Md., 1970, p 39. (b) Other references to stripping reactions appear in E. W. McDaniel, "Collision Phenomena in Ionized Gases," Wiley, New York, N. Y., 1964, Chapter 6.

(3) All experiments employed a Hitachi RMH-2 mass spectrometer, modified as previously described;⁴ the aniline spectrum was taken using 70-eV electrons, electron current 1 mA, source temperature 150°, source pressure 6×10^{-6} Torr, 8-kV ion acceleration, air as collision gas at 5×10^{-6} Torr pressure.

(4) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 313 (1969).