CIDNP Kinetics from Fourier Transform NMR[1]

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Abstract: Equations are derived for the kinetic analysis of Fourier transform (FT) NMR measurements of chemically induced dynamic nuclear polarization (CIDNP). The "polarized intermediate" model of Walling and Lepley is used. The equations account for the effects of the pulse angle, θ, and the pulse repetition time, τ, of the FT experiment, and the fact that the measured CIDNP magnetization is permanently destroyed. The derivation considers two cases: $\theta = 90°$, and $\theta \neq 90°$. Because of the complexity of the equations for $\theta \neq 90°$, it is not profitable to use intermediate pulse angles to study the kinetics of CIDNP reactions. The solution for $\theta = 90°$ is extended to experiments where accumulation of signal is necessary, as in natural abundance ^{13}C NMR. The equations relate the time dependence of the observed NMR intensity to the kinetic parameters of the reacting system in the general form, $I = C_1 + C_2 \exp(-C_3 f(t))$. where C_3 is the reaction rate constant. If T_1 is known, the enhancement factor, α/β, may be obtained from C_1 and C_2.

Chemically induced dynamic nuclear polarization (CIDNP) has become an important technique for the study of free-radical reactions in solution.[2] Theoretical treatments, based on the radical pair model, have provided insight about the origin of the phenomenon. They allow mechanistic interpretation of the emission and enhanced absorption signals which arise from the reaction-induced nonequilibrium, or non-Boltzmann, populations of nuclear spin states.

The kinetic aspects of CIDNP have also received attention.[3] To our knowledge, all CIDNP kinetic studies have been carried out using continuous wave (CW) NMR spectrometers, by repeatedly scanning the spectral region of interest to obtain the signal intensity as a function of time. Depending on the reacting system, the kinetic analysis of such data can be fairly straightforward. A report dealing with Fourier transform (FT) NMR measurements of spin-lattice relaxation times (T_1) in reacting systems briefly mentions ^{13}C CIDNP kinetic results.[4]

This paper deals with the application of Fourier transform NMR[5] to kinetic studies of systems displaying CIDNP. Specifically, it describes the changes which must be made in the previous CIDNP kinetic approaches to accommodate those features of FT NMR which are not normally encountered in CW NMR. These are the flip angle, θ, the pulse repetition time, τ, and signal accumulation. The resulting equations account for their effects and allow kinetic analysis of CIDNP data obtained by FT NMR.

Ernst and co-workers have shown that intensity anomalies can arise in FT NMR spectra of homonuclear-coupled spin systems which have non-Boltzmann populations.[6] Such effects are not included in the present treatment. They are not a factor, of course, in natural abundance carbon-13 and nitrogen-15 FT NMR of nonequilibrium spin systems.

Development of the Kinetic Expressions

The Kinetic Model. The key step in extracting kinetic information from experimental data is to relate the observable to the desired rate constants through a suitable expression based on a kinetic model. The observable in an NMR experiment is the intensity of the NMR signal of a reactant or product. For a given spectrometer under normal conditions, the intensity is directly proportional to the concentration of the compound. The proportionality constant may be called the apparent NMR absorption coefficient.

In the CIDNP effect the emission or enhanced absorption signal is actually due to a nonequilibrium population of nuclear spin states. Thus, a rigorous analysis of the dynamic situation may proceed through a description of the population of nuclear energy levels. While this approach has been applied to CIDNP kinetics,[3b,c,f] it is convenient, as Walling and Lepley showed,[3a] to consider the abnormal intensity to be due to an intermediate or "polarized" species. This species has an NMR absorption coefficient different from the one associated with normal product. In essence the two approaches are the same, both seeking to relate the increase in net magnetization observed in the sample to the responsible kinetic process. Both lead to similar kinetic expressions which yield rate constants and "enhancement" factors.

This work follows the "polarized" intermediate approach. The kinetic model will be the simplest reaction sequence which could display CIDNP, that of two consecutive first-order reactions (eq. 1). The reactant R, by some free-radical path, forms polarized intermediate P*, with rate constant k. The intermediate relaxes (returns to normal Boltzmann populations of nuclear spin states) to product P, with nuclear relaxation rate constant, $k_r = 1/T_1$. We first discuss the expressions derived for the CW experiment and then show the changes which are required to treat the FT experiment.

$$\mathrm{R} \xrightarrow{k} \mathrm{P}^* \xrightarrow{k_r} \mathrm{P} \qquad (1)$$

The CW Experiment. In the CW CIDNP experiment, it is assumed that a measurement does not perturb the spin populations. This is a reasonable approximation if the rf power of the spectrometer is kept well below saturation level ($\gamma^2 H_1{}^2 T_1 T_2 \ll 1$). As will be seen later, the FT experiment can mimic the CW experiment by use of a very small flip angle.

For the reaction in eq 1, if α and β are the NMR absorption coefficients of P* and P, respectively, the intensity observed at any time for an NMR line of P is[3a]

$$I_t = \alpha[\mathrm{P}^*]_t + \beta[\mathrm{P}]_t \qquad (2)$$

Taking R_0 as the initial concentration of R, solving the rate equations for [P*] and [P] gives the intensity in terms of the kinetic parameters of R and P* (eq 3a).

$$I_t = \frac{\alpha k}{k_r - k} R_0 (e^{-kt} - e^{-k_r t}) + \beta\left[R_0 - \frac{k_r R_0}{k_r - k} e^{-kt} + \frac{k R_0}{k_r - k} e^{-k_r t}\right] \qquad (3a)$$

Or, by collecting terms with common factors,

$$I_t = \beta R_0 + \frac{R_0}{k_r - k}(\alpha k - \beta k_r) e^{-kt} + \frac{k R_0}{k_r - k}(\beta - \alpha) e^{-k_r t} \qquad (3b)$$

which can be rewritten in the form of eq 3c.

$$I_t = A + Be^{-kt} + Ce^{-k_r t} \tag{3c}$$

The five constants (A, B, C, k, and k_r) in eq 3c may be obtained with a computer curve fitting program if sufficient experimental data are available. An independent check of the computer fit may be made by comparison of the value of T_1 ($=1/k_r$) so obtained with the value obtained by direct measurement.[7] Since R_0 is known and k and k_r are obtained explicitly in the curve fitting, the values of α and β are determined by the constants A, B, and C. The enhancement factor is defined as α/β.

If the steady state approximation is made for [P*], eq 3 simplifies to eq 4.[3a]

$$I = \beta R_0 + \left(\alpha \frac{k}{k_r} R_0 - \beta R_0\right)e^{-kt} \tag{4}$$

At this point in their derivation Walling and Lepley[3a] define $I_\infty = \beta R_0$ so that eq 4 may be rewritten

$$\ln\left(\frac{I - I_\infty}{I_\infty}\right) = \ln\left(\frac{\alpha}{\beta}\frac{k}{k_r} - 1\right) - kt \tag{4a}$$

I_∞ is the observed intensity at the completion of the reaction and was an observable quantity in their system. However, many reactions, especially photoreactions, do not go to completion in a reasonable time, or the signal itself may not be observable.

The problem of obtaining a value at "infinite" time occurs frequently, for example, in NMR relaxation time measurements,[7] and is best handled by computer fitting. The logarithmic approach to solving equations such as eq 4a is not always reliable because the errors involved are not characteristic of the measured quantities.[8,9] With the increasing availability of computers and curve fitting routines, the use of the exponential form of the equation is preferred for the least-squares fitting.[10]

The FT Experiment. In FT NMR the free induction decay (FID), or time response of a nuclear spin system to a high power rf pulse, is recorded and Fourier transformed to give the frequency domain NMR spectrum. In principle all the necessary information is contained in one FID.

In order to improve the signal-to-noise ratio, however, it is general practice to accumulate a number of FID's in a multichannel digital memory before the Fourier transformation. This is especially true in work with dilute solutions or with nuclei of low natural abundance such as ^{13}C or ^{15}N. This accumulation takes time. Any kinetic analysis of accumulated FT NMR data must account for the events occurring during this time.

In addition to accumulation time there are two other parameters of the FT NMR experiment which are important in the analysis of CIDNP kinetic data. They are the flip angle, θ, and the pulse repetition time, τ.

The following discussion will first briefly describe the role played by θ and τ.[11] Then it will show how the equations used for the CW CIDNP kinetics are modified to include θ and τ, resulting in an expression which gives the intensity measured at any pulse for $\theta = 90°$ and $\theta \neq 90°$. Finally, our treatment of the accumulation procedure will be described for the case, $\theta = 90°$.

The flip angle is the angle through which M, the net magnetization oriented along the Z axis of the magnetic field, is rotated toward the X-Y plane. For any angle θ the measurable signal in the X-Y plane is $M(\sin\theta)$ and the magnetization remaining aligned with the Z axis is $M(\cos\theta)$. After the pulse, the rotated magnetization is restored along the Z axis by natural relaxation processes governed by T_1, the spin-lattice relaxation time.

But T_1 processes can restore only a natural (Boltzmann) magnetization; an amount $M(1 - \cos\theta)$ of the abnormal magnetization arising from the CIDNP process is lost once it is sampled by the pulse.

At the next pulse the CIDNP contribution to M will come from two sources. The first is the magnetization which was unaffected by the previous pulse. This is not simply $M(\cos\theta)$ which remained after the previous pulse, but is $M(\cos\theta)e^{-\tau/T_1}$. The exponential term accounts for nuclear relaxation, from the non-Boltzmann condition, occurring during the interval τ. The second CIDNP contribution is that which forms under control of the chemical kinetics of the reaction during the time between pulses. Note that for a 90° pulse the first of these contributions is zero since all of M due to CIDNP is lost with each 90° pulse.

The importance of the pulse repetition time, τ, is now evident. The pulse repetition time must be long enough to allow sufficient chemical reaction, but short enough to prevent major loss of CIDNP intensity by nuclear relaxation.

CIDNP Kinetics in the FT NMR/Experiment. It is important to remember at this point that the net magnetization is proportional to concentration. Therefore we will refer to the effects of θ and τ on the concentrations of P* and P, understanding that [P*] and [P] represent a collection of nuclear spins.

The starting point for deriving the expressions for the analysis of CIDNP kinetics in the FT NMR experiment is eq 2. As in the CW experiment the concentrations of P* and P are needed as a function of time.

The case of $\theta = 90°$ will be considered first since it is conceptually easier. This is because *all* of the Z magnetization is destroyed with each pulse. The case of arbitrary angle θ will be treated later.

θ = 90°. Consider again the reaction (eq 1)

$$\mathrm{R} \xrightarrow{k} \mathrm{P}^* \xrightarrow{k_r} \mathrm{P} \tag{1}$$

The reaction is initiated at $t = 0$ and the total NMR signal intensity develops following eq 3. After time τ, the rf pulse is applied and the FID is recorded. With a 90° pulse all of M is rotated into the XY plane. During the next pulse interval M grows through two mechanisms: (a) through the formation of new P*; and (b) through longitudinal relaxation of P from the XY plane. For each pulse the measured FID will consist of contributions from P* formed *only during the preceding pulse interval* and from P which has been formed during the entire period from $t = 0$.

The amount of P* present at pulse n is then

$$[\mathrm{P}^*]_n = \frac{k}{k_r - k}[\mathrm{R}]_{n-1}(e^{-k\tau} - e^{-k_r\tau}) \tag{5}$$

Here $[\mathrm{R}]_{n-1}$ represents a pseudoinitial concentration for the formation of P* after pulse $n - 1$, and τ is the pulse repetition time. Clearly, $[\mathrm{R}]_{n-1} = R_0e^{-k(n-1)\tau}$, where $(n - 1)\tau$ is the total time from the start of the reaction to pulse $n - 1$.

The amount of P at pulse n is taken to be the amount of P formed up to and including pulse $n - 1$.

$$[\mathrm{P}]_n = R_0 - R_0e^{-k(n-1)\tau} \tag{6a}$$

The contribution made by P to the intensity measured at pulse n depends on τ and T_1. That is, not all of P will have recovered from the previous pulses. Only a fraction of it will be measurable at pulse n. This effective concentration is

$$[\mathrm{P}]_{\mathrm{eff}} = [R_0 - R_0e^{-k(n-1)\tau}](1 - e^{-\tau/T_1}) \tag{6b}$$

Note that the contribution to the intensity measured at pulse n from the P which forms by relaxation of P* between

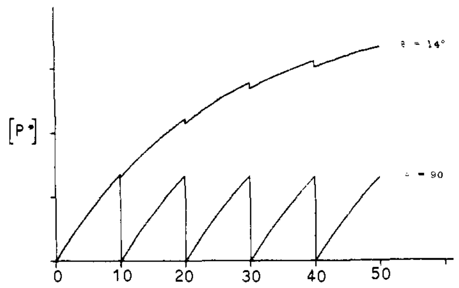

Figure 1. Time dependence of [P*] during early stages of a hypothetical reaction following eq 1 under the influence of the FT NMR experiment. The curves are for two different values of flip angle, θ, and the following other parameters: $\tau = 10$ s, $k = 10^{-4}$ s^{-1}, $k_r = 4 \times 10^{-2}$ s^{-1} ($T_1 = 25$ s), $R_0 = 1$ M.

pulses $n - 1$ and n is neglected. But the loss of intensity due to the relaxation of P* during that time is not neglected. This is important, for α is orders of magnitude larger than β.

Thus, for a 90° flip angle the intensity measured at pulse n is

$$I_n = \frac{\alpha k}{k_r - k} R_0 e^{-k(n-1)\tau} (e^{-k\tau} - e^{-k_r\tau}) + \beta[R_0 - R_0 e^{-k(n-1)\tau}](1 - e^{-\tau/T_1}) \quad (7)$$

Equations 3 and 7 represent the measured intensity of a single measurement at the two extremes of the value of the flip angle, θ. They represent the CW experiment ($\theta \approx 0°$) and the FT experiment for $\theta = 90°$.

One of the interesting features of the 90° pulse analysis is that maximum "concentration" or measurable magnetization due to the "polarized intermediate" occurs at the first pulse if τ is shorter than $\tau_{\max}$, the time at which the concentration of intermediate reaches maximum value in the two-step consecutive first-order scheme.[12] This is evident from the form of eq 5 in which the only variable, $[R]_{n-1}$, is continually decreasing with time. Hence, the familiar growth decay curve of the reacting intermediate is not followed. For $\theta = 90°$ the time dependence of [P*] is illustrated by the lower sawtooth of Figure 1, with teeth of ever decreasing height.

$\theta \neq$ **90°.** When θ is not 90° the expressions for [P*] and [P] become more complex. The statements that all magnetization due to P* is destroyed with each pulse and that $[P] = [R_0 - R_0 e^{-k(n-1)\tau}]$ are no longer valid. P is now forming via two routes: by relaxation of rotated P*, and by T_1 relaxation of P* which is "unaffected" by the pulse. The fraction of magnetization which is rotated is $\sin\theta$ and this fraction remains constant through the experiment. The time dependence of [P*] is closely related in this case to the first term in eq 3a with the modification that every τ seconds an amount $(1 - \cos\theta)[P^*]$ is removed, i.e., immediately converted to P.

The concentration of P* just before (−) and just after (+) a pulse is given in eq 8 for the first three pulses.

$$[P^*]_{1-} = \frac{kR_0}{k_r - k}(e^{-k\tau} - e^{-k_r\tau}) \quad (8a)$$

$$[P^*]_{1+} = [P^*]_{1-}(\cos\theta) \quad (8b)$$

$$[P^*]_{2-} = [P^*]_{1+} e^{-k_r\tau} + \frac{kR_0}{k_r - k} e^{-k\tau}(e^{-k\tau} - e^{-k_r\tau}) \quad (8c)$$

$$[P^*]_{2+} = [P^*]_{2-}(\cos\theta) \quad (8d)$$

$$[P^*]_{3-} = [P^*]_{2+} e^{-k_r\tau} + \frac{kR_0}{k_r - k} e^{-k2\tau}(e^{-k\tau} - e^{-k_r\tau}) \quad (8e)$$

$$[P^*]_{3+} = [P^*]_{3-}(\cos\theta) \quad (8f)$$

The first term on the right in eq 8c and 8e represents the amount of P* left at the end of each pulse interval due to loss by nuclear spin relaxation during that interval. The second term accounts for new P* formed during each interval. The constant term, $[kR_0/(k_r - k)](e^{-k\tau} - e^{-k_r\tau})$, can be represented by R'. Thus, $[P^*]_{3-}$ is given by eq 9.

$$[P^*]_{3-} = R'e^{-k2\tau} + e^{-k_r\tau}(\cos\theta)(R'e^{-k\tau} + e^{-k_r\tau}(\cos\theta)(R')) \quad (9a)$$

$$[P^*]_{3-} = R'e^{-k2\tau} + R'e^{-k\tau}e^{-k_r\tau}(\cos\theta) + R'e^{-k_r 2\tau}\cos^2\theta \quad (9b)$$

$$[P^*]_{3-} = \sum_{j=0}^{j=3-1} R'e^{-k(2-j)\tau}e^{-k_r j\tau}(\cos^j\theta) \quad (9c)$$

$$[P^*]_{n-} = \sum_{j=0}^{j=n-1} R'e^{-k(n-1-j)\tau}e^{-k_r j\tau}(\cos^j\theta) \quad (10)$$

Equation 10 represents the concentration of P* just before the nth pulse. Figure 1 shows the initial time dependence of [P*] calculated for two values of the flip angle.

The expression for $[P]_{n-}$ is given by eq 11. Note that this equation does not take into account previously pulsed P

$$[P]_{n-} = R_0 - [R]_n - [P^*]_{n-} \quad (11a)$$

$$[P]_{n-} = R_0 - R_0 e^{-kn\tau} - [P^*]_{n-} \quad (11b)$$

which has not returned to nuclear equilibrium. This can be accounted for by expressing $[P]_{n-}$ in terms of the amount present at pulses $n - 1$ and n as in eq 12. The P from relaxation of newly formed P* is neglected.

$$[P]_{n-} = \{R_0 - [R]_{n-1} - [P^*]_{(n-1)-} + (1 - \cos\theta)[P^*]_{(n-1)-}\}(1 - e^{-\tau/T_1}) + ((e^{-k_r\tau})[P^*]_{(n-1)+}) \quad (12)$$

Now the intensity measured at any pulse, n, is

$$I_n = (\alpha[P^*]_{n-} + \beta[P]_{n-})\sin\theta \quad (13)$$

Because of the complexity of eq 10 and 12, the numerical evaluation of eq 13 is a formidable task, even when all of the kinetic parameters of the reaction are known or assumed. Thus it is of little value to use intermediate pulse angles to study the *kinetics* of CIDNP reactions, even without accumulating signals. If θ is small ($\theta < 15°$) then $(1 - \cos\theta) \approx 0.03$ while $\sin\theta \approx 0.25$, and the results might be treated as a CW experiment (eq 3).[13]

Effect of Accumulating Pulses. It is common practice in ^{13}C FT NMR to accumulate a number of FID's in order to obtain a reasonable signal-to-noise ratio. Since in a CIDNP kinetic experiment the time dependence of the signal intensity is of interest, it is necessary to accumulate the signal in a manner which can be related to the reaction time coordinate. This can be done by separately accumulating successive intervals of the reaction and analyzing the results as follows. For a pulse angle of 90°, each of the i data collections will consist of the sum of N accumulations of individual intensities given by eq 7 and can be expressed as

$$I_i^{\text{total}} = \sum^{N}\left\{\frac{\alpha k}{k_r - k} R_0 e^{-k(n-1)\tau}(e^{-k\tau} - e^{-k_r\tau}) + \beta[R_0 - R_0 e^{-k(n-1)\tau}](1 - e^{-\tau/T_1})\right\} \quad (14)$$

Rearrangement of eq 14 to collect terms with the time factor, $e^{-k(n-1)\tau}$, gives eq 15.

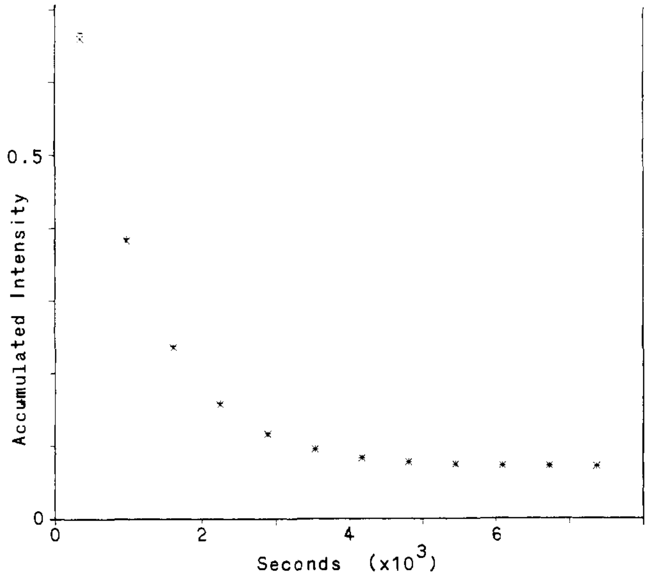

Figure 2. Simulation of NMR intensity vs. time for a CIDNP reaction (eq 1) studied by accumulative FT NMR. Each point represents the signal obtained from the accumulation of 64 FID's and is plotted at the midpoint of the collection period. The + are for the exact solution (eq 15) and the × are for the approximate solution (eq 16a). The parameters used in the calculation are $\theta = 90°$, $\tau = 10$ s, $k = 10^{-4}$ s^{-1}, $k_r = 4 \times 10^{-2}$ s^{-1}, $R_0 = 1$ M, $\alpha = 500$, and $\beta = 1$.

$$I_i^{\text{total}} = \left\{\frac{\alpha k}{k_r - k} R_0(e^{-k\tau} - e^{-k_r\tau}) - \beta R_0(1 - e^{-\tau/T_1})\right\} \sum_n^{n'} e^{-k(n-1)\tau} + N\beta R_0(1 - e^{-\tau/T_1}) \quad (15)$$

In eq 15, $n = (i - 1)N + 1$, and $n' = iN$. The lower limit of the summation for each collection interval is the index of the initial pulse for that interval. Therefore, $n = 1, N + 1, 2N + 1, \ldots$, for collection intervals $i = 1, 2, 3, \ldots$. Hence, the total time from the start of the reaction, $t = (n - 1)\tau$, appears in the exponent.

Although eq 15 accurately describes the accumulated intensity, it is not useful for analyzing the actual experiment. This is because the summation contains not a single time, but N times. Therefore we replace the summation with the product $Ne^{-kg(t)}$, where $g(t)$ is the time from the *start* of the reaction to the *midpoint* of collection period i.

$$I_i^{\text{total}} = NR_0\beta(1 - e^{-\tau/T_1}) + NR_0\left\{\frac{\alpha k}{k_r - k}(e^{-k\tau} - e^{-k_r\tau}) - \beta(1 - e^{-\tau/T_1})\right\}e^{-kg(t)} \quad (16a)$$

or

$$I_i^{\text{total}} = C_1 + C_2 e^{-C_3 g(t)} \quad (16b)$$

This replacement introduces very little error. Figure 2 is a plot of the exact (eq 15) and approximate (eq 16) solutions for a given set of parameters. The difference at early stages of the reaction is ~1% and quickly becomes much smaller.

A computer fit of the experimental data to eq 16b yields the three constants C_1, C_2, and C_3. The reaction rate constant, k, is C_3. When T_1 is known, C_1 and C_2 give β and α, respectively.

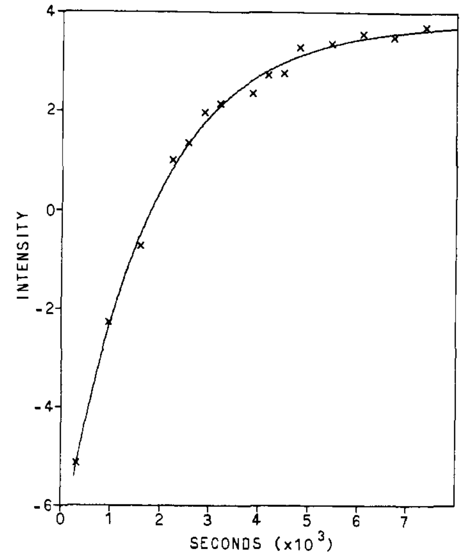

Figure 3. Relative measured intensity of the ^{13}C NMR peak of benzene obtained via accumulative FT NMR during photodecomposition of benzoyl peroxide in chloroform. Each × represents the accumulation of 64 FID's ($\tau = 10$ s) and is plotted at the midpoint of the collection period. The line represents the computer fit of these points to eq 16b.

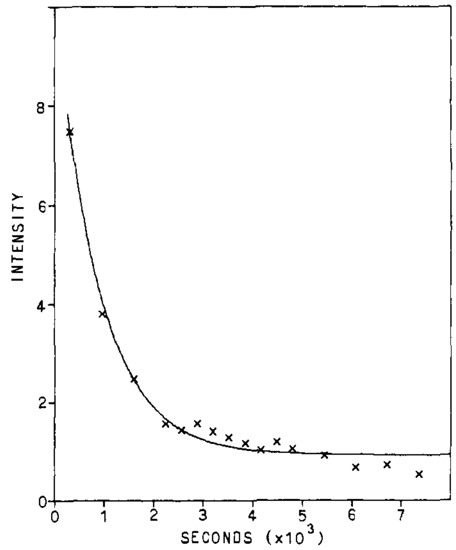

Figure 4. Relative measured intensity of the ^{13}C NMR peak of C-1' carbon of phenyl benzoate obtained via accumulative FT NMR during photodecomposition of benzoyl peroxide in chloroform. Each × represents the accumulation of 64 FID's ($\tau = 10$ s) and is plotted at the midpoint of the collection period. The line represents the computer fit of these points to eq 16b.

Comparison of the CW and FT Kinetic Experiments. In comparing the CW and FT cases, eq 3 and 16, the major difference is that the CW case yields k_r directly from the computer fit. The FT experiment does not yield k_r directly because the effect of the pulse is to make T_1-controlled processes τ dependent and not t dependent. Fortunately the chemistry of the reaction is not affected by the physics of the experiment and the chemical rate constant remains t dependent. The fact that the FT kinetic approach does not explicitly yield a value for T_1 does not present any serious difficulty since there are other ways of measuring relaxation times.

Also, there is a question of whether relaxation times differ for compounds in a reacting system such as CIDNP as opposed to the nonreacting system. A shortening of T_1 may occur if the radical flux is high. This problem is likely to be important in studies of fluorine or proton CIDNP during thermally induced decompositions. Christensen et al. found no significant reductions of ^{13}C T_1's in their measurements of relaxation times during the thermal decomposition of benzoyl peroxide.[4]

It is apparent from the analyses presented here that the accuracy of CW kinetic measurements can be severely compromised if the condition of negligible saturation is not met. The rf power levels must be explicitly evaluated and controlled in CW CIDNP kinetic studies. A corresponding pitfall exists in the $\theta = 90°$ FT kinetic experiment. Deviation from an exact 90° pulse will leave a residual Z magnetization component and lead to inaccurate results.

Example. We applied the FT kinetic method described here in a study of ^{13}C CIDNP occurring during the photoinduced decomposition of benzoyl peroxide (BPO) in chloroform.[14] We used accumulative ^{13}C FT NMR and analyzed the CIDNP of benzene and phenyl benzoate. The main difference in the working versions of eq 16 is that the term $k/(k_r - k)$, which describes the simple first-order nature of the model reaction, eq 1, must be replaced by more complex combinations of rate constants.[14] Also, both terms of eq 16 must be multiplied by the fraction of reactant which forms a given product.

A computer fit of the CIDNP data to eq 16b gave the results shown in Figures 3 and 4.[14] The rate constants for photodecomposition of BPO in $CHCl_3$ were 6.1×10^{-4} s^{-1} from benzene data and 4.6×10^{-4} s^{-1} from phenyl benzoate data. Rate constants obtained from parallel chemical analyses were 0.7×10^{-4} s^{-1} and 1.2×10^{-4} s^{-1}, respectively.[14] The agreement is quite good and illustrates the usefulness of the method.

Extension of this approach to other complex systems should not be difficult. The important step is to write expressions for the concentrations of P* and P. Relaxation from the non-Boltzmann condition is always first order. In the 90° case the effect of the flip angle is easily worked in. The T_1 effects during the time between pulses are straightforward. Equations can then be written for the reasonable reaction paths and data fit to them to find the best solution.

Acknowledgment. We thank Dr. Henry Resing for helpful discussions on nuclear relaxation.

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(12) K. B. Wiberg, "Physical Organic Chemistry", Wiley, New York, N.Y., 1964, p 323.

(13) The case of the arbitrary angle might be improved if the stepwise synthesis of the time dependence of $[P^*]$ (eq 10) could be replaced by the solution of $d[P^*]/dt = k[R] - k_r[P^*] - f(t)[P^*]$, where $f(t)$ contains the effects of the pulse angle and interval. This function should contain a constant, depending on θ and a step function of period τ. The proper form of $f(t)$ has so far eluded us.

(14) C. F. Poranski, Jr., W. B. Moniz, and S. A. Sojka, *J. Am. Chem. Soc.*, **97**, 4275 (1975).