# Photolysis of Butane-2,3-dione in Fluorocarbon Solvents; a Chemically Induced Nuclear Polarization (CIDNP) Study

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CIDNP observations of the polarized signals from products of radical reactions in solutions of neat butane-2,3-dione in perfluorocyclohexane and perfluorodecalin, and in solutions with added radical scavenger or hydrogen donor, are consistent with three primary processes. There are symmetric (probably) and unsymmetric fragmentation and hydrogen-abstraction by triplet butane-2,3-dione from the starting material, and each yields free radicals. In all solutions the mechanisms of ensuing reactions are suggested. In the presence of $CCl_4$ and $CCl_3Br$ pair substitution effects dominate the CIDNP behaviour. When high concentrations of propan-2-ol are present evidence is given for reaction of the excited singlet state of the parent molecule.

THE photochemistry and photophysics of butane-2,3-dione have received wide attention in the gas phase and in solution and the molecule finds frequent use in photochemistry as a sensitizer or quencher. Absorption of u.v. light leads to an excited singlet state and from it, *via* inter-system crossing, an excited triplet. Luminescence is observed from both states and extensive studies of fluorescence and phosphorescence quenching have been made.[1-5] Alcohols quench the phosphorescence but not the fluorescence whereas phenols and amines quench both.[5] With triethylamine as quencher it has been shown that the triplet state alone leads to significant radical formation.[6]

In several gas-phase studies [7-9] product analysis has given clear evidence of photo-fragmentation and three primary processes have been suggested: symmetric scission to two acetyl radicals, formation of methyl radicals and carbon monoxide, and production of acetyl and methyl radicals and carbon monoxide. The latter may occur in consecutive steps *via* an unstable intermediate $CH_3CO\dot{C}O$ radical. The gas-phase data are consistent with the overall third process [9] but a low-temperature solid state e.s.r. investigation showed that fragmentation to $CH_3CO\dot{C}O$ and methyl was not the only primary process.[10]

In solution further complications occur by virtue of reaction of the triplet with hydrogen sources to produce the ketyl radical or the radical anion; these may be in acid-base equilibrium or have a common predecessor in an exciplex. Both radicals have been observed directly using e.s.r. spectroscopy.[6,11-14] A surprising observation [13] is that the ketyl may be produced in an initially electron-spin-polarized state in alcohol solutions although the rate of hydrogen abstraction expected would seem too low to compete with electron relaxation in the triplet precursor; the fact that the anion observed in the presence of triethylamine (1 mol $dm^{-3}$) in alcohol solutions is unpolarized [6] seems more consistent with expectations although the rate of hydrogen abstraction is faster than in pure alcohol solutions. The anion is observed in both *cis*- and *trans*-forms. It has been suggested that various primary radicals add directly to biacetyl to generate secondary ones.[6,11,15] Spin-trapping has provided direct evidence of the existence of acetyl radicals even in situations which favour direct hydrogen-abstraction,[6] showing that photo-fragmentation occurs also.

Product studies in cyclohexane, diethyl ether, dioxan, ethylbenzene, and propan-2-ol solutions [16] have suggested the presence of acetyl and ketyl radicals as well. In benzene solution products were consistent with a primary dissociation into acetyl radicals only but in the presence of aldehydes evidence was obtained for ketyl radicals too.[17] In hexane solution at wavelengths below 310 nm enol formation was observed.[18] Of particular relevance to this work, an investigation in inert fluorocarbon and fluoroether solvents showed little reaction at 298 K but the quantum yield rose one-hundred fold at 373 K.[19] Methane, ethane, and carbon monoxide were detected as products and the reaction was discussed in terms of a primary dissociation to acetyl radicals followed by some subsequent disproportionation to methyl and carbon monoxide.

It is apparent that butane-2,3-dione has a complex chemistry in solution involving radicals produced from one or more fragmentation routes and from hydrogen-abstraction from suitable substrates. This chemistry appears poorly understood and in view of the photochemical importance of the molecule it was decided to investigate it using the chemically induced dynamic nuclear polarization (CIDNP) technique. With a system of this complexity this yields qualitative rather than quantitative results and it is impossible to determine the relative importance of the different reaction routes. The basic solvents used have been two fluorocarbons, perfluoromethylcyclohexane (PP2) and perfluoro-1-methyldecalin (PP9), which are inert to radical attack. Initially, solutions in neat solvents were studied and reaction mechanisms devised. These were then tested firstly by addition of radical scavengers to remove the products of radicals diffusing out of their original cages and secondly by addition of hydrogen donors to eliminate any self-abstraction reactions and to accentuate the hydrogen-abstraction route. The scavengers used, $CCl_4$ and $CCl_3Br$, were chosen to produce one common secondary radical ($\cdot CCl_3$) to yield similar products and assist n.m.r. peak assignment.

As in previous experiments,[20-22] products were present at extremely low concentration and could not be extracted for identification (their equilibrium n.m.r. signals were usually too small to be observed). Extreme dilution shifts made identification of products from their n.m.r. chemical shifts difficult and CIDNP peaks were identified wherever possible by independent experimentation with possible products at similar concentrations; when these were not available recourse was made to chemical intuition and assignments were tested for consistency with Kaptein's rules.[23] Use of fluorocarbon solvents led to the further complication that many of the products were only sparingly soluble, and irradiated solutions became cloudy.

A feature of the approach taken has been the quantitative calculation of the relative polarizations expected either from different products or from different protons inside one product. This has been essential in understanding why some peaks are observed and others not. In our experiments low precursor concentrations are used to obtain maximum radical concentrations in the vicinity of the receiver coil. Different CIDNP peaks maximise at different times after the commencement of irradiation due to different relaxation and reaction rates. Approximate lifetimes of the signals are indicated in the Results section.

## EXPERIMENTAL

Experiments were conducted using a Varian A60A spectrometer as described previously.[20] Focused light from a 500 W high-pressure mercury lamp was directed on to a silica light-pipe and internally reflected into the solution contained inside a normal n.m.r. tube; the pipe fitted into the tube and the two were spun together. Sample purity was crucial to the observation of CIDNP in the butane-2,3-dione system. The fluorocarbons were obtained from Fuorochem. Ltd. and de-oxygenated by passage of nitrogen for 30 min before use. All other chemicals used were degassed through several freeze–pump–thaw cycles before vacuum distillation. Solutions were made up, sealed into the tubes with ' parafilm ' around the light-pipe, and kept for brief periods under nitrogen in a glove box before use.

The concentration of butane-2,3-dione was adjusted for maximum radical concentration at the receiver coil. Assuming that the radical concentration is directly proportional to the light intensity this occurs when the substrate concentration is $(2.303\ \varepsilon l)^{-1}$, where $\varepsilon$ is the decadic extinction coefficient and $l$ the distance between the end of the light-pipe and the receiver coil of the spectrometer. With $l = 0.5$ cm this implies an optimum concentration of 0.039 mol dm$^{-3}$ for butane-2,3-dione and this did yield the optimum CIDNP intensities. Because several peaks were shortlived it was necessary to scan spectra a small amount at a time.

## RESULTS

CIDNP spectra observed during the photolysis of deoxygenated solutions of butane-2,3-dione in PP2 and PP9 are shown in Figure 1 and the peaks are listed in Table 1, along with their observed polarizations; their assignments follow later since many depend upon mechanistic arguments. Some of the peaks were of very small intensity, but they were reproducible and vanished on cessation of irradiation except for the parent peak which returned almost to its initial intensity. Peaks H and I were most clearly observed in PP9, for solubility reasons, and persisted for a very short time: they could be observed only by starting field-scans very close to their positions. Bubbles of gas were observed in the irradiated solutions.

In the presence of tetrachloromethane the spectrum change, shown in Figure 2, was obtained with a scavenger concentration approximately twice that of the substrate; the peaks are listed in Table 1. Of the original peaks only the absorption A, the emission B, and the emission of butane-2,3-dione remained, and all at lower intensity, suggesting that these may have originated in cage processes. Three new peaks appeared which reflect reaction with tetrachloromethane.

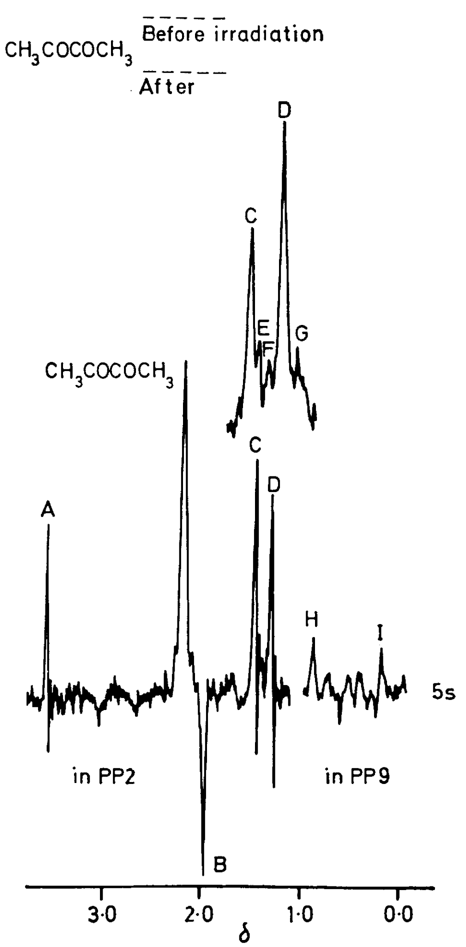


FIGURE 1 CIDNP spectra in the irradiation of 0.035 mol dm$^{-3}$ butane-2,3-dione in PP2 and PP9, including a horizontal scale expansion of the region near δ 1.4. The bottom trace is a composite, the lines H and I being observed most clearly in PP9 solution. The time indicated is that at which the sweep (from the start of the trace) was commenced at a rate of 4 Hz s$^{-1}$ after illumination started

Similarly in the presence of a more efficient radical scavenger CCl$_3$Br (at various concentrations) only peaks A, B, and the parent remained with the emission of the latter decreasing significantly as the scavenger concentration increased. Peak L was observed in common with the CCl$_4$ system and a new peak (M) was observed (Figure 3 and Table 1).

TABLE 1

| Peak | Pure PP2/PP9 | | $+CCl_4$ | | $+CCl_3Br$ | | +MeOH | | $+Me_2CHOH$ ($<0.1$ mol dm$^{-3}$) | | $+Me_2CHOH$ ($>0.1$ mol dm$^{-3}$) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Shift/ δ | Phase, time/s | Shift/ δ | Phase, time/s | Shift/ δ | Phase, time/s | Shift/ δ | Phase, time/s | Shift/ δ | Phase, time/s | Shift/ δ | Phase, time/s |
| MeCOCOMe | 2.18 | E, 300 | 2.18 | E, 300 | 2.18 | E, 200 * | 2.18 | E, 300 | 2.18 | E, 300 | 2.18 | E, 300 |
| A | 3.58 | A, 20 | 3.58 | A, 20 | 3.58 | A, 20 | | | | | | |
| B | 1.98 | E, 90 | 1.98 | E, 30 | 1.98 | E, 30 | 1.98 | E, 30 | 1.98 | {E →A, , 300 | 1.98 | A, 300 |
| C | 1.47 | A, 180 | | | | | 1.47 | A, 180 | 1.47 | A, 200 | 1.47 | A, 200 |
| D | 1.31 | A, 180 | | | | | 1.31 | A, 180 | 1.31 | A, 200 | ? | |
| E | 1.43 | A, 30 | | | | | ? | | | | | |
| F | 1.38 | A, 30 | | | | | ? | | | | | |
| G | 1.24 | A, 30 | | | | | | | | | | |
| H | 0.90 | A, 20 | | | | | | | | | | |
| I | 0.21 | A, 20 | | | | | | | | | | |
| J | | | 2.46 | A, 30 | | | | | | | | |
| K | | | 2.31 | E, 30 | | | | | | | | |
| L | | | 1.75 | E, 90 | 1.75 | E, 90 | | | | | | |
| M | | | | | 2.65 | A, 50 | | | | | | |
| N | | | | | | | 1.40 | A, 180 | | | | |
| $Me_2CHOH$ | | | | | | | | | 1.18 | E, 300 | 1.18 | E, 300 |
| P | | | | | | | | | | | 1.36 | A, 200 |
| R | | | | | | | | | | | 1.28 | A, 120 |
| S | | | | | | | | | | | 1.16 | A, 120 |

* Dependent on concentration of $CCl_3Br$.

When solutions to which varying concentrations of methanol had been added where photolysed, further spectral changes occurred (Figure 4 and Table 1). The methanol peaks were not polarized and, compared with the original spectrum, lines A, G, H, and I were missing. A new strong absorption was observed at a shift value which would obscure peaks E and F, if they were present.

Further experiments were performed in the presence of a more efficient hydrogen-donor, propan-2-ol, which proved unusually soluble in PP2 and allowed solutions of up to 0.2 mol dm$^{-3}$ in alcohol to be studied. Solutions containing low concentrations ($<0.1$ mol dm$^{-3}$) showed different behaviour

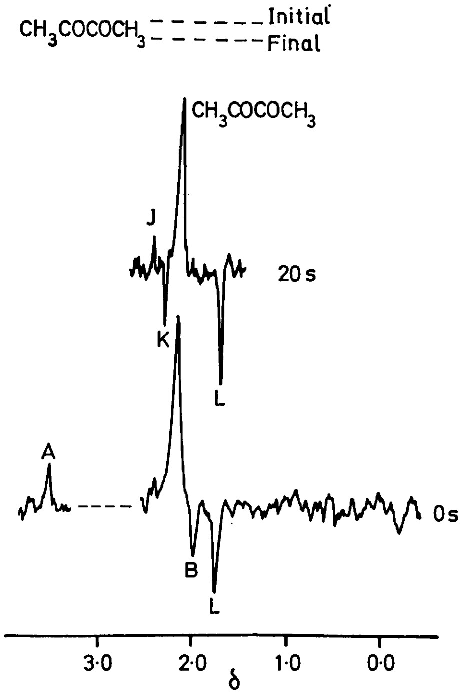


FIGURE 2 Spectra of 0.035 mol dm$^{-3}$ butane-2,3-dione in 0.081 mol dm$^{-3}$ $CCl_4$ in PP2. The time between the start of irradiation and the commencement of each trace, swept at the previous rate, is shown. The initial and final equilibrium peak heights refer to the lower traces. Note the absence of peaks around δ 1.4

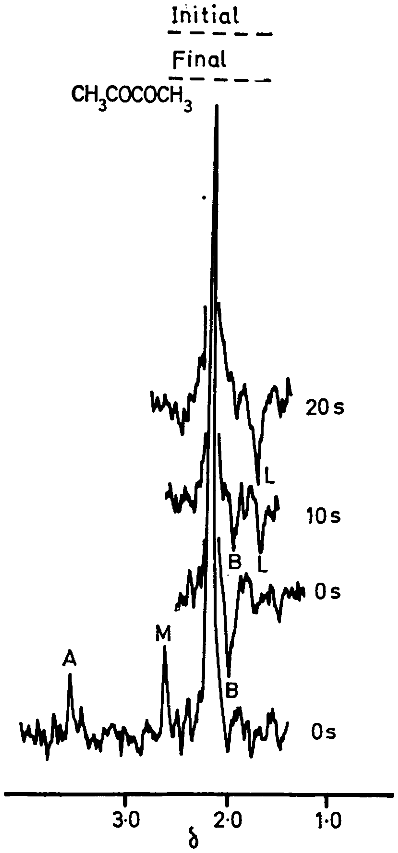


FIGURE 3 Spectra from 0.40 mol dm$^{-3}$ butane-2,3-dione in 0.06 mol dm$^{-3}$ $CCl_3Br$ in PP2. Note the small amount of emission of the parent peak. In each spectrum the final peak height given is that of the equilibrium signal observed sufficiently long after 60 s of irradiation for polarization to have relaxed. Timing conventions are as before

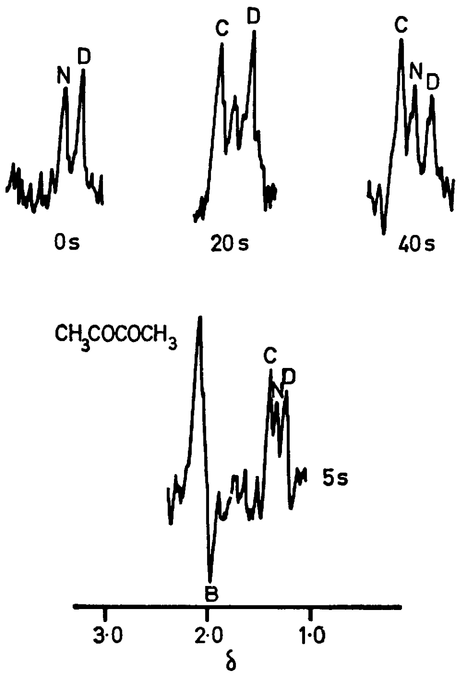


FIGURE 4 The spectrum from 0.037 mol dm$^{-3}$ butane-2,3-dione in 0.07 mol dm$^{-3}$ methanol in PP2. The parent peak had a strong emissive component and the relative intensities of the C, N, and D peaks varied greatly in the first 40 s of illumination, as shown in the expanded upper traces of this region

(Figure 5) from those which contained higher ones (Figure 6). At low concentration peak B was in emission for about 20 s but then changed to absorption and the butane-2,3-dione and C and D peaks were more strongly polarized than in the initial experiments without added scavenger or donor. All the polarization was comparatively long-lived and there was less bubble formation. The methyl protons of propan-2-ol itself were polarized. After irradiation considerable loss of starting material was apparent and peak B was observed at equilibrium. At high concentrations of propan-2-ol B appeared in extremely strong absorption and three new peaks were observed, one of which had a shift extremely close to that of line D whose presence is consequently unconfirmed. Again the final spectrum showed considerable depletion of butane-2,3-dione and a signal at B.

## ASSIGNMENT AND DISCUSSION

The observation of emissive polarization from butane-2,3-dione throughout shows that it is reformed during irradiation, and in a cage process. Peak A in the olefinic region is assigned to the methylene protons in the enol $CH_2{=}C(OH)COCH_3$; this was confirmed by its disappearance from solutions through which HCl gas was bubbled to catalyse the tautomerism. Peak B is assigned to acetone, H to ethane, and I to methane by comparison with sample spectra. Consideration of the peaks C—G allows assignment of D to the equivalent methyl groups in $CH_3COC(OH)(CH_3)_2$ but shows, particularly from lack of multiplicity, the absence in pure butane-2,3-dione solutions of $CH_3COCH(OH)CH_3$ and $CH_3COCOCH_2CH_3$ products.

In the presence of tetrachloromethane their shifts identified peaks J and K to $CH_3COCl$ and $CH_3COCCl_3$ respectively whilst with $CCl_3Br$ peak M originates in $CH_3CCl_3$. Peak L, observed in the presence of both scavengers, is probably a product of the reaction of $\cdot CCl_3$ radicals. These experiments imply that peaks C—I of the unscavenged system originate in scavenge products from radicals escaping from their cages. All other assignments were made on the basis of mechanistic arguments and Kaptein's rule for net polarization [23] (no multiplet polarization was observed) [equation (i)],

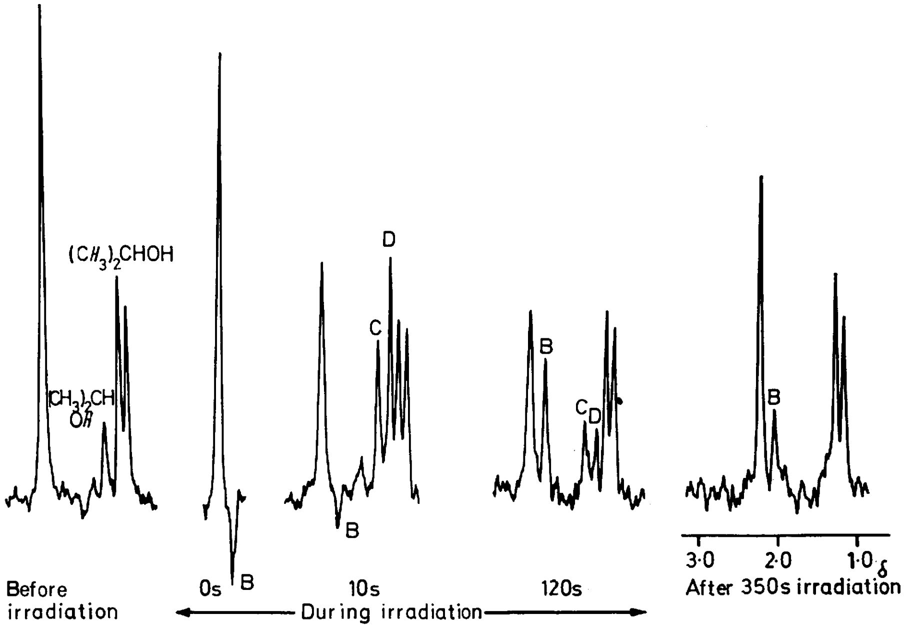


FIGURE 5 Spectra from 0.39 mol dm$^{-3}$ butane-2,3-dione with 0.05M propan-2-ol in PP2. Included are spectra before and after irradiation, showing considerable loss of intensity in the parent peak and an equilibrium acetone signal (B). Note that the phase of the polarized line B changes during the irradiation

where $\mu$ is positive for a triplet or freely diffusing ' F-pair ' precursor and negative for a singlet one, $\varepsilon$ is positive for cage recombination products and negative for scavenged ones, $\Delta g$ is positive for the radical with the higher $g$-value, and $A_i$ is the sign of the hyperfine coupling constant to nucleus i on the radical being considered.

$$\Gamma = \mu\varepsilon A_i \Delta g \qquad \text{(i)}$$

The observed polarization $\Gamma$ is positive for absorption and negative for emission.

Previous studies have shown that intersystem crossing from the excited singlet ($n \longrightarrow \pi^*$) formed on irradiation to the lowest triplet state is a fast [24] ($k$ *ca.* $4 \times 10^7$ $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$) and efficient ($\Phi$ *ca.* 1) process and that triplet quenching proceeds at a diffusion-controlled rate with quenchers whose triplet energies are below that of butane-2,3-dione.[25] The triplet nature of the reactive species in our experiments was confirmed by addition of benzil to $CCl_4$ and PP2 solutions in neither of which was CIDNP observed. The parameter $\mu$ is consequently positive throughout (although see later for strong propan-2-ol solutions).

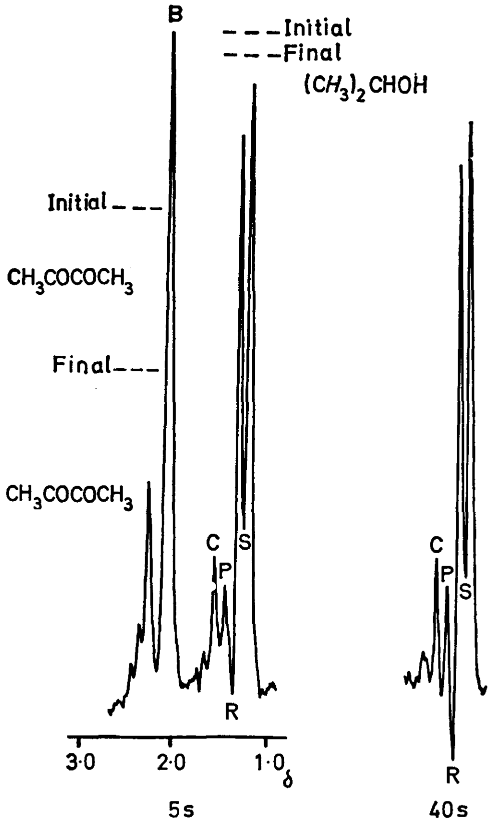


FIGURE 6 Spectra of 0.042 mol $\mathrm{dm^{-3}}$ butane-2,3-dione in 0.15 mol $\mathrm{dm^{-3}}$ propan-2-ol in PP2. Note the extremely large absorptive polarization of the acetone peak (B); this peak was visible at equilibrium after cessation of irradiation, as in Figure 5. The presence of the emissive doublet formed by peaks R and S is seen most clearly in the spectrum started 40 s after irradiation commenced. The propan-2-ol peaks have a weak emissive component during irradiation

The e.s.r. characteristics of the radicals which may be present in our systems are listed in Table 2.[25] The $g$-values of two are unknown; that of $CH_3CO\dot{C}O$ was taken to be similar to that of acetyl whilst that of $\cdot CH_2COCOCH_3$ was considered to be less than that of $CH_3CO\dot{C}(OH)CH_3$, by comparison with similar species. Small or zero values of hyperfine couplings to, *e.g.* $\gamma$ protons implies that these will not be spin-polarized when the radicals form products.

The sign of the parameter $\varepsilon$ can be obtained consequently from the observed sign of $\Gamma$ and allows mechanistic conclusions to be made.

To rationalise the observation of peaks A, B, and the butane-2,3-dione emission in the solutions in the absence of added hydrogen donors three primary processes are required, each leading to different polarized cage products. In all reaction schemes below radical pairs are denoted by a bar and the polarized species are labelled with asterisks (*); the emission (E) or absorption (A) predicted from Kaptein's rule is indicated but comment is made only where these predictions differ from the observations. The primary processes are in (1) and (2a) or (2b). In the alternatives (2a) or (2b) loss of CO does not affect the spin correlation of the radical pair.

TABLE 2

| Radical | $g$-Value | $A_H$/G [a] |
|---|---|---|
| $CH_3\dot{C}O$ | 2.0005 | $A_\beta$ positive |
| $CH_3CO\dot{C}O$ | | $A_\gamma$ 0 |
| $\cdot CH_2COCOCH_3$ | | $A_\alpha$ negative |
| $\cdot CH_3$ | 2.002 52 | $A_\alpha$ −23.04 |
| $(CH_3)_2\dot{C}OH$ | 2.003 17 | $A_\beta$ +19.66, $A_{OH}$ +0.70 |
| $\cdot CH_2OH$ | 2.003 34 | $A_\alpha$ −17.38, $A_{OH}$ +1.15 |
| $CH_3CO\dot{C}(OH)CH_3$ | 2.004 57 | $A_\beta$ +13.41 |
| $\cdot CCl_3$ | 2.0091 | |

[a] 1 G = $10^{-4}$ T.

$$\mathrm{CH_3COCOCH_3{}^{T}} \longrightarrow \overline{\mathrm{CH_3CO\dot{C}O + \dot{C}H_3}} \longrightarrow \mathrm{CH_3COCOCH_3{}^{*E}} \qquad (1)$$

$$\mathrm{CH_3COCOCH_3{}^{T}} \longrightarrow \overline{\mathrm{CH_3CO\dot{C}O + \dot{C}H_3}} \longrightarrow \overline{\mathrm{CH_3\dot{C}O + \dot{C}H_3 + (CO)}} \longrightarrow \mathrm{CH_3COCH_3{}^{*E}} \qquad (2a)$$

$$\mathrm{CH_3COCOCH_3{}^{T}} \longrightarrow \overline{\mathrm{CH_3\dot{C}O + CH_3\dot{C}O}} \longrightarrow \overline{\mathrm{CH_3\dot{C}O + \dot{C}H_3 + (CO)}} \longrightarrow \mathrm{CH_3COCH_3{}^{*E}} \qquad (2b)$$

The absorption A can be rationalised only by attack on the ground-state molecule which acts as a hydrogen donor [reaction (3)]. This appears to be confirmed by the absence of peak A in the presence of better hydrogen donors.

$$\begin{gathered}\mathrm{CH_3COCOCH_3{}^{T} + CH_3COCOCH_3} \longrightarrow \\ \overline{\mathrm{CH_3CO\dot{C}(OH)CH_3 + \dot{C}H_2COCOCH_3}} \\ \downarrow \\ \mathrm{CH_3COCOCH_3{}^{*A} + CH_2{}^{*A}{=}C(OH)COCH_3} \qquad (3)\end{gathered}$$

The overall emission of the butane-2,3-dione peak shows that reaction (1) is the dominant path to its polarization. A possible alternative to reaction (3), combination of the radicals in a cage process, would lead to a product with peaks in the C—G region but no such peaks are observed in the presence of radical scavengers and this process appears negligible.

These reactions imply the following diffusing radicals which may react before or after they lose their initial polarization by relaxation: $\dot{C}H_3{}^{*A}$, $CH_3{}^{*A}\dot{C}O$, $CH_3CO\dot{C}O$, $CH_3\dot{C}OC(OH)CH_3{}^{*E}$ and $CH_3COCO\dot{C}H_2{}^{*E}$.

With acetyl, methyl reacts in an F-pair to produce emissive acetone (B); the importance of this route, besides reaction (2), was evident from the decrease in emission intensity in the presence of radical scavengers. Reaction of any radical with $CH_3CO\dot{C}O$ is unlikely owing to the latter's instability. With the ketyl, methyl

$$\dot{C}H_3 + CH_3CO\dot{C}(OH)CH_3 \longrightarrow \overline{\dot{C}H_3 + CH_3CO\dot{C}(OH)CH_3} \longrightarrow CH_3COC(OH)(CH_3{}^{*A})_2 \quad (4)$$

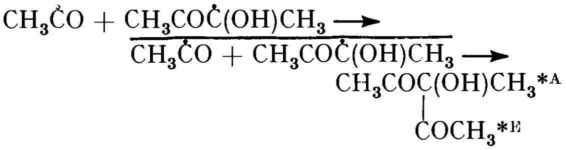
yields a product to which peak D is assigned [reaction (4)]. Polarized ethane and methane result from memory effects [23,26] [reactions (5) and (6)]. No products

$$\dot{C}H_3{}^{*A} + \dot{C}H_3{}^{*A} \longrightarrow C_2H_6{}^{*A} \quad (5)$$

$$\dot{C}H_3{}^{*A} + CH_3COCOCH_3 \longrightarrow CH_4{}^{*A} + \dot{C}H_2COCOCH_3 \quad (6)$$

were observed of the latter radical with any others, which suggests it rapidly fragments, possibly to keten and acetyl although keten was not detected; its emissive polarization may have relaxed too quickly for observation.

Experiment is consistent with the addition of acetyl to the ketyl [reaction (7)].



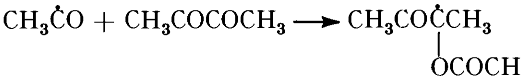
$$CH_3\dot{C}O + CH_3CO\dot{C}(OH)CH_3 \longrightarrow \overline{CH_3\dot{C}O + CH_3CO\dot{C}(OH)CH_3} \longrightarrow \underset{\displaystyle COCH_3{}^{*E}}{CH_3COC(OH)CH_3{}^{*A}} \quad (7)$$

The absorptively polarized methyl is assigned to peak C, the effect of this cage process dominating any possible memory-effect polarization in the product. The emissive methyl would occur in the region of the spectrum where it would be likely to be obscured by the butane-2,3-dione and acetone resonances; its presence was not confirmed. Any memory-effect absorptive polarization produced in butane-2,3-dione by combination of polarized acetyl radicals was dominated by emission produced in cage reaction (1). There was no evidence for hydrogen abstraction by acetyl from the starting material.

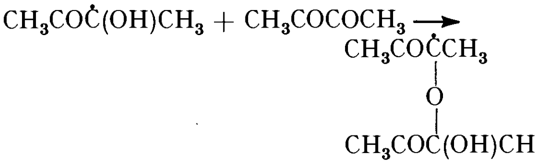
At this stage peaks E, F, and G, due to scavenge products, are still unassigned, and nor is it possible to assign them by consideration of the reactions of the ketyl radical not yet considered. Reactions of any radicals with $CH_3CO\dot{C}O$ and $\cdot CH_2COCOCH_3$ have been discounted already (and, independently, consideration of possible products with ketyl and their polarizations make any identification of peaks E, F, and G untenable). There remain only three possible memory-effect polarizations to yield emissive polarizations. Hydrogen abstraction by ketyl from starting material would yield either acetoin (not observed) or emissively polarized butane-2,3-dione [indistinguishable from that produced by reaction (1)]. Dimerisation may well occur but if it does so it is too slow a process to compete with nuclear relaxation for no emission is observed in the relevant region of the spectrum.

It would seem that the peaks E, F, and G cannot arise from reactions of the primary radicals and we seek their origins in the reactions of secondary radicals formed from the primary ones. These seem most likely to be formed by the reactions (8)—(10).

$$\dot{C}H_3 + CH_3COCOCH_3 \longrightarrow CH_3CO\dot{C}(OCH_3)CH_3 \quad (8)$$

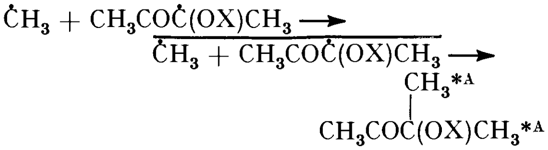


$$CH_3\dot{C}O + CH_3COCOCH_3 \longrightarrow \underset{\displaystyle OCOCH_3}{CH_3CO\dot{C}CH_3} \quad (9)$$

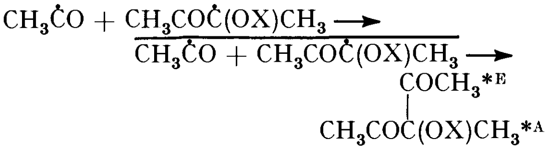


$$CH_3CO\dot{C}(OH)CH_3 + CH_3COCOCH_3 \longrightarrow \begin{array}{c} CH_3CO\dot{C}CH_3 \\ | \\ O \\ | \\ CH_3COC(OH)CH_3 \end{array} \quad (10)$$

Here we have assumed that the carbon-centred radicals are more probable than their oxygen-centred counterparts, in common with general experience. Addition radicals of this type with butane-2,3-dione have been postulated previously.[6,11,15] Writing the general structure as $CH_3CO\dot{C}(OX)CH_3$ the existence of absorptive E, F and G peaks can be rationalised by the reactions (11) and (12).



$$\dot{C}H_3 + CH_3CO\dot{C}(OX)CH_3 \longrightarrow \overline{\dot{C}H_3 + CH_3CO\dot{C}(OX)CH_3} \longrightarrow \overset{\displaystyle CH_3{}^{*A}}{CH_3COC(OX)CH_3{}^{*A}} \quad (11)$$



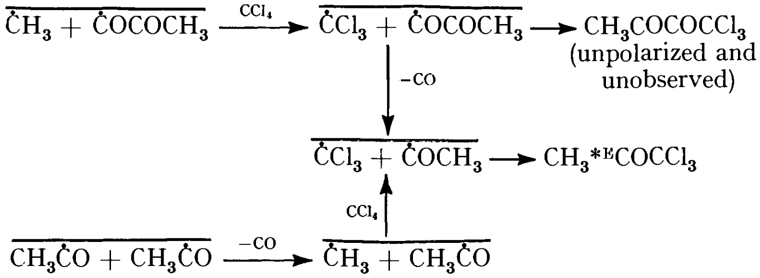
$$CH_3\dot{C}O + CH_3CO\dot{C}(OX)CH_3 \longrightarrow \overline{CH_3\dot{C}O + CH_3CO\dot{C}(OX)CH_3} \longrightarrow \overset{\displaystyle COCH_3{}^{*E}}{CH_3COC(OX)CH_3{}^{*A}} \quad (12)$$

Reaction (11), with the different possible constituents X, could in fact explain all three peaks E, F, and G (and possibly others hidden under the stronger lines) but (12) cannot be discounted; the emission from the $-COCH_3{}^{*E}$ may again be obscured by overlying peaks. It was not possible, however, to assign these three peaks exactly.

Although the purpose of adding radical scavengers was to aid the analysis of the system discussed above the detailed analysis of these systems shows that their effect was not simply to remove radicals diffusing from the original cages. In the first place, in all cases with added scavenger the overall CIDNP intensities from primary cage products were reduced from the pure state. This is consistent with the occurrence of radical pair substitution [27-30] due to scavenging being sufficiently rapid to interrupt the polarization-generating diffusion and re-encounter sequences. A new radical, in this case $\cdot CCl_3$, is formed which forms a substituted pair with the unscavenged member of the original geminate pair; the correlation of spins is preserved in the pair substitution process although the magnitude of polarization is affected.

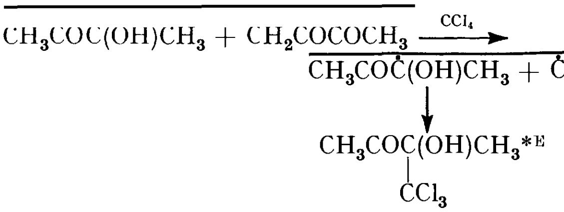
Both of the primary processes (1) and (2) occur to produce polarized butane-2,3-dione and acetone from the cage processes, but also in the presence of scavenger a competing rapid reaction with the methyl radical yields an identical substituted pair in each case, which itself yields a polarized product [reactions (13)].

These reactions predict emission from $CH_3{}^{*E}COCCl_3$ (peak K), as observed. The same prediction is made for F-pairs which probably also contribute. Similarly the primary process (3) still yields the enol resonance (A) but also pair substitution occurs [reactions (14)]. Again F-pair interaction would produce a qualitatively similar result. From its shift and phase, peak L is assigned to this product.



(13)

The pair-substitution effect probably dominates F-pair ones since the immediate products $CH_3Cl$, $CH_3COCl$, and $CH_3COCOCH_2Cl$ are unpolarized and not observed. The occurrence of cage polarization in the A, B, and butane-2,3-dione peaks does, however, imply that a small amount of polarized primary radical should escape from the cage. In the case of solutions containing $CCl_4$ memory-effect polarized $CH_3{}^{*A}COCl$ is produced in this way but no similarly polarized products were detected from $\cdot CH_3$ or $CH_3CO\dot{C}(OH)CH_3$ radicals. For methyl this may have been due to too rapid nuclear relaxation whilst for the ketyl, besides this possible explanation, schemes (3) and (14) predict generation of opposite polarizations from different cage processes.

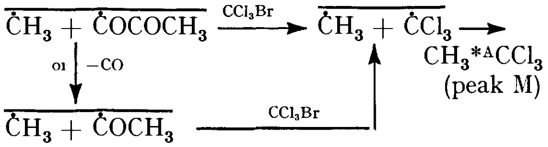


(14)

These general rationalisations acquire further credence when the results of the more efficient radical-scavenger $CCl_3Br$ are considered in detail. Here the emission in butane-2,3-dione disappeared almost completely owing to a very fast pair-substitution process. However $CH_3{}^{*E}COCCl_3$ (peak K) was not observed and this suggests that the dominant pair substitution in primary scheme (1) was as in reactions (15). This implies that methyl reacts more readily with $CCl_4$ than does $CH_3\dot{C}O$-$CO$ or $CH_3\dot{C}O$, but the converse is true for $CCl_3Br$. That reaction of unsubstituted methyl and acetyl pairs still occurs to a reduced amount is evidenced by the emissive acetone resonance. The absence of $CH_3{}^{*E}CO$-$CCl_3$ indicates [*via* scheme (2), if this is important] that loss of CO by acetyl competes with the pair-substitution process.

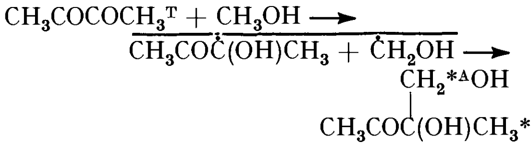
In contrast, the enol polarization (A) and the emission from peak L show that reaction scheme (14) still occurs, as would be expected. No memory-effect polarization was observed from $CH_3COCBr(OH)CH_3$, the expected scavenge product of diffusing ketyl radicals, again probably owing to reaction not competing with spin relaxation.

Despite the added complication of pair-substitution effects the polarization observed in the presence of radical scavengers is entirely consistent with the three primary processes suggested in their absence. As a further check we proceed to discuss the results in the presence of the hydrogen donors methanol and propan-2-ol, chosen as compromises between their hydrogen-donating abilities and the simplicities of their n.m.r. spectra. We should expect process (3) to diminish in importance in their presence. First we discuss the methanol results.



(15)

The over-riding feature is the disappearance of enol peak A and the increase in the emission from butane-2,3-dione itself, entirely consistent with the replacement of process (3) by (16). The absorption N is assigned to the polarized methyls in this product but the polarized methylenes were not observed. However a detailed calculation of the expected relative intensities of these two polarizations, using basic CIDNP theory,[31,32] shows that the intensity of the methylenes should be 0.22 of that of the methyls. With the signal-to-noise ratio of the observed spectra (Figure 4) this is entirely consistent with our ability to observe one but not the other. The alternative primary processes (1) and (2) were still operative, methanol being too insoluble in fluorocarbons to favour reaction (16) completely. Reactions between F-pairs of ketyl radicals with methyl and acetyl led to



(16)

products and polarizations C and D, as above. Polarized methane and ethane were not observed probably because of the increased ketyl concentration in this solution, and nor were the products from the addition reactions (11) and (12) observed for the same reason. This explains the absence of peaks E, F, and G in methanol-containing solutions, although E and F would in fact be obscured by the new peak N. Other absences were polarized methanol, which might have been expected from reaction of $\cdot CH_2{}^{*E}OH$ with methanol *via* a memory process, and polarized products from reaction of this radical with methyl and acetyl. Hydroxymethyl may consequently have disappeared through hydrogen abstraction from, or addition to, the parent molecule. Again the former might have produced memory-polarized methanol but the latter would yield a carbon-centred radical expected to react through hydrogen abstraction without producing polarization. The absence of acetoin as a polarized product indicates negligible reaction between the ketyl radical and either hydroxymethyl or methanol. Once again behaviour in the presence of methanol is consistent with the originally suggested primary processes.

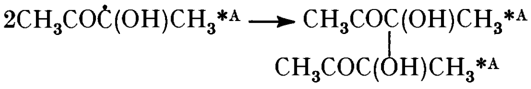
With propan-2-ol the situation was more complex although at low concentrations ($<0.1$ mol dm$^{-3}$) the behaviour was entirely consistent with that in the presence of methanol with the exception that the acetone resonance appeared first in emission and subsequently became absorptive. At high concentrations acetone appeared in greatly enhanced absorption. In all solutions the enol resonance, A, was absent, showing the unimportance of primary process (3) but reactions (1) and (2) still occurred as demonstrated by the emission of the parent peak and the initial emission from acetone at low propan-2-ol concentration (any emission at higher concentration was dominated by the very strong absorption). The change with time from emission to absorption suggests a second, overall slower, route to polarized acetone. Furthermore in this system the rate of consumption of butane-2,3-dione was increased by ten-fold over the pure solution and led to observable acetone at equilibrium after irradiation; the peak height of acetone roughly correlated with the loss of intensity from propan-2-ol.

To rationalize these observations, and the appearance of extra polarized lines, it is necessary to invoke reaction of propan-2-ol with singlet butane-2,3-dione [reactions (17)]. Although the singlet reaction itself would have to be very fast to compete with intersystem crossing it is not unreasonable to suggest that the overall reaction rate to polarized acetone differs from that of route (2). This scheme immediately allows assignment of the emission peaks R and S to the spin-coupled methyl of acetoin. An absolute calculation of expected CIDNP intensities suggested that the magnitude of the polarization in acetone should be 4.5 times that in acetoin, and is consistent with our inability to detect acetoin (in a region of other, absorptive, peaks) in low concentrations of propan-2-ol. This unusual observation of singlet-state reactivity was confirmed by direct experiment.

$$CH_3COCOCH_3{}^{S} \xrightarrow{(CH_3)_2CHOH} \overline{CH_3CO\dot{C}(OH)CH_3 + (CH_3)_2\dot{C}OH}^{\,S} \longrightarrow CH_3COCH(OH)CH_3{}^{*E} + CH_3{}^{*A}COCH_3{}^{*A} \qquad (17)$$

A saturated solution of benzil in PP2 ($1 \times 10^{-3}$ mol dm$^{-3}$) was made up to 0.035 mol dm$^{-3}$ in butane-2,3-dione and one half was made 0.12 mol dm$^{-3}$ in propan-2-ol. The two solutions were investigated separately. In the absence of propan-2-ol no CIDNP was observed on irradiation and there was no evidence for reaction, but in its presence acetone was observed in absorption and the acetone doublet in emission with intensities similar to those in the absence of benzil. Benzil quenches butane-2,3-dione by energy transfer at a diffusion-controlled rate [2] (*ca.* $10^{10}$ mol dm$^{-3}$ s$^{-1}$ in our solutions) whilst the rate of triplet quenching by hydrogen abstraction from alcohols is in the range [5] $10^3$—$10^7$ mol dm$^{-3}$ s$^{-1}$. At the reactant concentrations used if the reaction proceeded through a triplet state the polarization should have been reduced by a factor of 8.4 in the presence of benzil and the phase should have been inverted. Neither was observed and we conclude that butane-2,3-dione does react in its singlet state with propan-2-ol to yield radical products.

Other reactions in the propan-2-ol systems include dimerisation of acetoin radicals to yield polarized product, to which peak P is assigned, in a memory effect [reaction (18)].



$$2CH_3CO\dot{C}(OH)CH_3{}^{*A} \longrightarrow \begin{array}{c} CH_3COC(OH)CH_3{}^{*A} \\ | \\ CH_3COC(OH)CH_3{}^{*A} \end{array} \qquad (18)$$

Assignment of this peak was substantiated by comparison with equilibrium signals from the same molecule produced by irradiation with sunlight.[33] In addition polarized propan-2-ol was produced by the exchange reaction (19), although the emission observed was not

$$(CH_3{}^{*E})_2\dot{C}OH + (CH_3)_2CHOH \longrightarrow (CH_3{}^{*E})_2CHOH + (CH_3)_2\dot{C}OH \qquad (19)$$

strong. There was no CIDNP evidence for dimerisation of $(CH_3{}^{*E})_2\dot{C}OH$ radicals or for their reaction with methyl or acetyl. However with a singlet initiation step the polarizations produced in radicals diffusing from singlet cages and F-pair ones would be opposite and they may have cancelled, and also relaxation may again have been effective. The absence of polarized products from these reactions is inconclusive. Addition of this radical to the ketyl was apparently unimportant as compared with reaction (17). Once more no memory-polarized products of the reactions of polarized methyl and acetyl radicals were detected.

## CONCLUSIONS

In solutions in inert solvents butane-2,3-dione undergoes three primary photochemical processes summarized in equations (1)—(3). There is no direct evidence that the symmetric scission occurs (2b) but the observation of emissively polarized parent material from reaction (1) makes the conditions for producing polarized acetone by reaction (2a) more stringent although such competing cage reactions are known.[21] This conclusion is consistent with previous work.[10] It is apparent that five primary radicals result and the ensuing chemistry is complex with radical–radical combinations, radical-atom abstraction reactions, and radical addition to parent molecules all occurring. Although CIDNP provides the basic evidence for such processes, the chemistry it discloses is unlikely to be complete for only polarized species are detected. Unless memory effects occur, atom-abstraction and the recombinations of identical radicals do not produce observable peaks. However some points are apparent in the general radical chemistry: $CH_3CO\dot{C}O$-$\dot{C}H_2COCOCH_3$ radicals are too unstable to show any products from freely diffusing species and only affect primary cage processes. Methyl and acetyl radicals appear to react at substantially different rates with $CCl_4$ and with $CCl_3Br$. Although peaks E, F, and G have not been identified completely it is apparent that they do not result from the reactions of any of the five primary radicals, and further secondary radicals have to be postulated. Throughout peak assignment was hampered by a wide range of possible products having very similar chemical shift values and it may well be that not all polarized products have been detected.

The relative importance of the various reaction pathways is impossible to assess save to note that few of the compounds suggested here have been reported in product-analysis studies, although it is reassuring that the formation of enol has been noted previously.[18] As mentioned above the amount of product from our irradiations is so small as to preclude normal analysis. We note too that many of the compounds suggested are themselves photoactive and it is of little surprise that they have not been reported in long-term irradiations, regardless of their primary quantum yields.

Radical-pair substitution has been shown to exert a profound effect on the CIDNP spectra observed in the presence of radical scavengers and it is probable that this occurs often when attempts are made to distinguish between cage and diffusion products of radical reactions in the way reported here.

The reaction of excited singlet-state butane-2,3-dione with propan-2-ol is one of only a few such observations of reactions of singlet states although there are theoretical reasons for suggesting that the inherent reactivities of the $S_1$ and $T_1$ states of carbonyl compounds should be similar.[34] Studies of both acetone[35] and adamantanone[36] reactions with propan-2-ol have provided direct evidence for this. Ours appears to be the first report of butane-2,3-dione giving radical reaction products following reaction of its excited singlet state.

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