

- agreement in the calculated electron populations with those calculated with 631G\*\* basis set.
- (29) Potts, A. W.; Lempka, H. J.; Streets, D. G.; Price, W. C. *Philos. Trans. R. Soc. London, Ser. A*. **1970**, *268*, 59. Potts, A. W.; Williams, T. A.; Price, C. W. *Faraday Discuss. Chem. Soc.* **1972**, *54*, 104. The compounds included in Figure 11 are methane, ethane, methyl fluoride, methyl chloride, methanol, and methylamine.
- (30) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J.; Brundle, C. R.; Kuebler, N. A. *J. Am. Chem. Soc.* **1976**, *98*, 7179.
- (31) Hammett, L. P. "Physical Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1970; p 374 ff.
- (32) Bernardi, F.; Bottoni, A.; Eplotis, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 7205.
- (33) Another way in which to compare the hydrogen electron populations for methane and methyl fluoride makes use of the calculated populations from the proton to infinity, which are 0.517 for methane and 0.507 for methyl fluoride. The hydrogen populations may be approximated as twice this value, or 1.034 and 1.014 e, respectively. The difference, 0.020 e, agrees with the value given in Table IV.
- (34) Lone-pair interactions have received extensive study; Wolfe, S.; Schlegel, B.; Whangbo, M.-H. *Can. J. Chem.* **1974**, *52*, 3787. Wolfe, S.; Rauk, A.; Tel, L. M.; Csizmadia, I. G. *J. Chem. Soc. B* **1971**, 136. Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371. The effect of lone-pair interactions on C-H stretching frequencies and bond lengths is reviewed: McKean, D. C. *Chem. Soc. Rev.* **1978**, *3*, 399.
- (35) Wiberg, K. B. *J. Am. Chem. Soc.* **1979**, *101*, 2204.
- (36) The effect of fluorine and lithium substitution on the electron populations in acetylene has been examined by Politzer and Harris (ref 23a), and the effect of methyl substitution on anions has been examined: Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 6572.
- (37) Binkley, J. S.; Whitehead, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. *QCPE* **1978**, *11*, 368.

## Nonexponential Proton Spin-Lattice Relaxation and Internal Rotation of Methyl Groups

E. Haslinger\* and W. Robien

Contribution from the Institut für Organische Chemie der Universität Wien, A-1090 Wien, Austria. Received July 16, 1979

**Abstract:** Nonexponential relaxation has been analyzed by direct observation of the null points of the two coincident components of a methyl signal after a 180° pulse. From these observations correlation times for both internal rotation of the methyl group and local reorientation were determined. The method has been used to study association behavior and internal mobility of medium and large molecules and to assign methyl resonances. This method is generally applicable to study internal mobility and solute-solvent interactions in medium or large molecules which are bearing methyl groups.

### Introduction

In an NMR experiment absorption of electromagnetic radiation by a spin system causes transitions from a lower to an upper energy level. The radiationless return to equilibrium requires radio-frequency power of the same energy which is provided by fluctuating magnetic fields. This process is called spin-lattice relaxation and is dependent on the details of the molecular motion.<sup>1</sup> It can be observed by measuring the time dependence of the longitudinal magnetization which is usually exponential and can be characterized by a relaxation time  $T_1$ . If the overall motion of a system of three or more spins is highly anisotropic, cross correlation may give rise to a nonexponential relaxation pattern and slows down the relaxation rate.<sup>5-8</sup> Therefore a number of papers have been devoted to the study of the relaxation behavior of methyl groups; however, only few observations of nonexponential spin-lattice relaxation in solutions have been reported.<sup>2-4</sup> In these cases the  $T_1$  decay has been analyzed as a sum of two exponentials by a nonlinear least-squares fit, which cannot be done very accurately.<sup>3,4</sup> Recently it has been shown that the two components of the longitudinal magnetization can be resolved and their individual relaxation rates have been measured.<sup>9</sup> After a 180° pulse the two components relax independently so that near the null point the faster relaxing component may be positive, while the other is still negative. In the extreme narrowing limit, they also have different  $T_2$  values, thus giving rise to a difference signal (Figure 1). From a series of these spectra the  $T_1$  values for both components and their relative contributions could be obtained.

We have used this method to investigate the internal mobility of methyl groups in several medium and large molecules.

### Theory

The theory of three relaxing spins ( $I = 1/2$ ) in an equilateral triangle has been treated in various degrees of sophistication.<sup>5-8</sup> Some of these models are too complex for our experiments, where the extreme narrowing approximation is valid and there are only three observed quantities. One has therefore to assume that the methyl group is rotating relative to an isotropically reorienting framework. It is known from the composite particle method of spectral analysis<sup>10-12</sup> that a methyl group is represented by a doublet and a quartet state. The total  $z$  magnetization is also made up of a doublet and a quartet component. These components have different relaxation rates, which are coupled together. They are therefore mixed into two components  $M_A$  and  $M_B$  with relaxation times  $T_1^A$  and  $T_1^B$ . If the extreme narrowing approximation is valid, the faster relaxing component has the shorter  $T_2$  value and hence the greater line width. Using the matrix elements given by Bain and Lynden-Bell<sup>13</sup> one can write the relaxation matrix in terms of the total magnetization ( $M_T$ ) which is the observed quantity and the difference between the doublet and the quartet magnetization:<sup>9</sup>

$$\frac{d}{dt} \begin{bmatrix} M_T \\ M' \end{bmatrix} = \begin{bmatrix} 10x' + 2\eta & -2\sqrt{3}x' \\ -2\sqrt{3}x' & 4x - 2x' + 6\eta - 5\eta \end{bmatrix} \begin{bmatrix} M_T - M_T^0 \\ M' \end{bmatrix} \quad (1)$$

$x$  is the contribution to the dipolar relaxation of the methyl protons, which is proportional to the time integral of the self-correlation function between proton pairs;  $x'$  is the contribution arising from the correlation between the dipolar coupling of

**Table I.** Results Obtained by Analysis of a Series of Difference Signals from the Compounds 1-4

compd	solvent concn, mol L <sup>-1</sup>	$T_1^A$ , s	$T_1^B$ , s	$y$	$\tau_C$ , ps	$\tau_M$ , ps	viscosity at 34 °C, cP
1-acetylpyrene (1)	CDCl <sub>3</sub> 0.41	3.28 ± 0.03	5.5 ± 0.3	0.35 ± 0.03	12 ± 0.5	1.4 ± 0.5	0.62
	CDCl <sub>3</sub> 0.35	3.69 ± 0.11	5.6 ± 0.3	0.34 ± 0.03	10 ± 1	2.5 ± 1	0.61
1-pyrenylacetic acid methyl ester (2)	CDCl <sub>3</sub> 0.36	2.68 ± 0.02	4.2 ± 0.5	0.06 ± 0.02	12 ± 1.5	7.0 ± 1.3	0.64
	C <sub>6</sub> D <sub>6</sub> 0.20	3.9 ± 0.1	4.3 ± 0.4	0.11 ± 0.02	6 ± 1	7.0 ± 2	0.60
etiobiliverdin (3)	CDCl <sub>3</sub> 0.11	0.68 ± 0.01	1.6 ± 0.1	0.13 ± 0.01	64 ± 2	12 ± 2	
		0.62 ± 0.01	1.7 ± 0.1	0.15 ± 0.03	76 ± 2	10 ± 3	
cobester (4) methyl signal 1 2 3,4 5 6 7	C <sub>6</sub> D <sub>6</sub> 0.02	1.02 ± 0.01	2.4 ± 0.2	0.085 ± 0.01	41 ± 3	12 ± 2	
		0.48 ± 0.02	2.5 ± 0.7	0.14 ± 0.03	113 ± 10	9 ± 5 <sup>a</sup>	
		0.62	2.5	0.13	80	10 <sup>b</sup>	
		0.71 ± 0.04	2.3 ± 0.4	0.12 ± 0.04	67 ± 8	10 ± 3	
		0.37 ± 0.02	2.5 ± 0.5	0.14 ± 0.02	152 ± 10	11 ± 4	
		0.37 ± 0.02	2.5 ± 0.5	0.14 ± 0.02	152 ± 10	11 ± 4	

<sup>a</sup> Only left side of signal fitted. <sup>b</sup> Estimated from the time duration of the signal splitting.

one proton with each of the other two and is proportional to the time integral of the cross correlation function.  $\eta$  and  $\eta'$  are the relaxations due to random fields and correlated random fields at pairs of nuclei. It has been shown that assuming the ratio of  $\eta'/\eta$  one can separate the random field contribution and derive two correlation times for the motion of the methyl groups:  $\tau_M$ , which is the correlation time about the motion of the methyl axis, and  $\tau_C$ , which is characterizing the reorientation of the axis.<sup>9</sup> The complete expressions for  $x$  and  $x'$  from ref 9 are

$$x = 0.3 \left( \frac{\mu_0}{4\pi} \right)^2 \hbar^2 \gamma^4 r_{HH}^{-6} \left[ \frac{3}{4} (\tau_C + \tau_M) + \frac{1}{4} \tau_C \right] \quad (2)$$

$$\frac{x'}{x} = \frac{2\tau_M^{-1} - \tau_C^{-1}}{2\tau_M^{-1} + 8\tau_C^{-1}} \quad (3)$$

where  $\mu_0$  is the permeability of the vacuum and  $r_{HH}$  is the interproton distance. If the type of reorientation is Debye diffusion,  $\tau_C^{-1} = 6D$  for the motion of the framework and  $\tau_M^{-1} = 4D_M$  for diffusional internal rotation. From these observations two functions  $y$  and  $z$  are derived:

$$z = (t_A^{-1} - t_B^{-1}) / 2(t_A^{-1} + t_B^{-1}) \quad (4)$$

$$Y = M_B^0 / (M_A^0 + M_B^0) \quad (5)$$

$t_A$  and  $t_B$  are measured null points of the A and B components and  $M_A^0$  and  $M_B^0$  are their relative contributions. From this one can get values for  $\eta/x$  and  $x'/x$  by a contour map<sup>9</sup> or by direct calculation. The value of  $x$  is determined using the equation

$$x = (t_A^{-1} + t_B^{-1}) \ln 2 / \left( 14 + 8\eta/x - 2\frac{x'}{x} - 4\frac{\eta'}{x} \right) \quad (6)$$

obtained from (1). Setting  $r_{HH} = 1.79 \text{ \AA}$  from (2) and (3) one obtains<sup>22</sup>

$$\tau_C = 2.5 \times 10^{-10} (x + 2x') \quad (7)$$

## Experimental Section

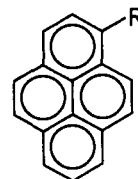
**Spin-Lattice Relaxation Experiments.** All inversion-recovery experiments were performed on a Varian XL-100-15 spectrometer. The system computer (Varian 620-L-100, 16K core) allowed acquisition of 8K data points. The transformed spectrum was thus represented by 4K (4096) data points (0.06 Hz per data point at 250 Hz spectral width). The shape of the resonance line was represented by 20-40 data points; these were stored, using a 2K transient recorder (Biomation Model 805) and transferred to a tape and via a Silent 700 ASR Texas Instruments Data terminal to a CDC Cyber 73 computer. With the two measured quantities  $t_A$  and  $t_B$  and a reasonable estimate for  $y$ , theoretical line shapes were computed and fitted to the experimental line shapes,<sup>21</sup> thus giving corrected values for  $t_A$ ,  $t_B$ , and  $y$ . All mea-

surements were made in sample tubes of 5-mm diameter. The solutions were carefully degassed by several freeze-pump cycles. The temperature in the probe was 34 °C and the field homogeneity was kept as high as possible. The deuterium resonance of the solvent served as field-frequency lock. The 90° pulse was 24  $\mu$ s.

An Ubbelohde viscosimeter was used for determination of the viscosity. Solutions of the substances at the same molar concentration but in nondeuterated solvents were measured at 34 °C.

To check that the measured effects are not caused by nonlinearity of the detector system or inhomogeneity of  $B_2$ , etc., we have carefully observed the CH<sub>2</sub> signal of compound 2. Although the CH<sub>3</sub> signal becomes clearly a difference signal near the null point, no change could be observed in the shape of the CH<sub>2</sub> resonance line. Moreover, this signal is relaxing exponentially. Furthermore, we have analyzed the relaxation of one of the ester methyl signals of 4 in a low-resolution experiment. Within the experimental error we obtained the same values for  $T_1^A$  and  $T_1^B$  as from the analysis of the difference signal.

**Materials.** The preparation of 1-acetylpyrene (1) is described in the literature.<sup>14</sup> 1-Pyrenylacetic acid methyl ester (2) was made by

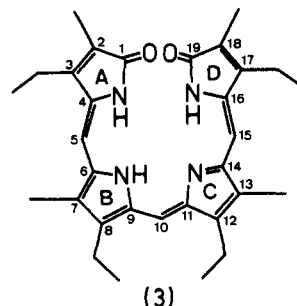


(1) R = COCH<sub>3</sub>

(2) R = CH<sub>2</sub>COOCH<sub>3</sub>

adapting the procedure of McKillop et al.<sup>15</sup> with Tl(NO<sub>3</sub>)<sub>3</sub> as follows: 0.01 mol of 1 dissolved in 150 mL of methanol was added to a solution of 0.011 mol of TTN in 25 mL of methanol containing 7.5 mL of 70% perchloric acid. The thallium(I) nitrate was removed by filtration, the filtrate diluted with water, and the product extracted with chloroform. After drying and filtering through a short column of alumina using chloroform as eluent, 2 was obtained by evaporation (95% theory).

Etiobiliverdin (3) was kindly supplied by Professor H. Falk (Uni-



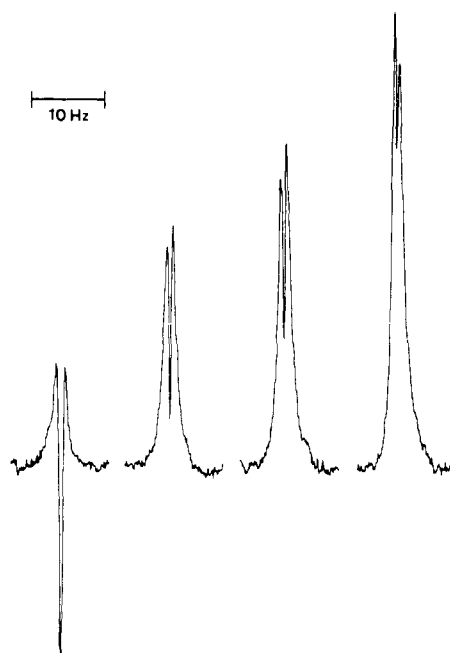
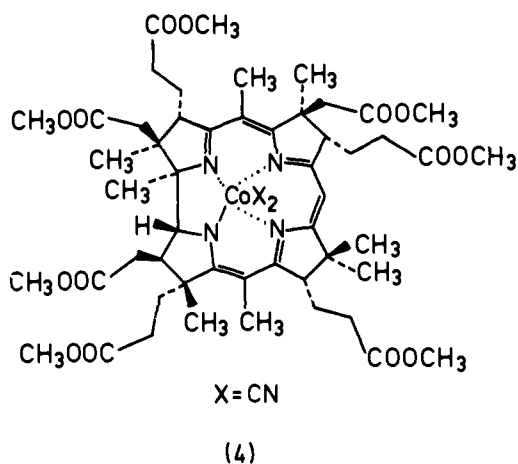


Figure 1. Resonances of the methyl groups situated on the rings B and C in etiobiliverdin (3) 0.48, 0.50, 0.53, and 0.57 s after the 180° pulse.

versity of Vienna) and the sample of cobester (4) was a generous gift from Professor A. R. Battersby (University Cambridge).



## Results and Discussion

We have analyzed the nonexponential methyl relaxation of the compounds 1–4. Table I gives the values of  $\eta'$ ,  $T_1^A$ , and  $T_1^B$ . The values for  $\tau_C$  and  $\tau_M$  are calculated assuming  $y' = 0$ . If dipolar relaxation is dominant,  $x'/X$  deduced from the observations depends little on the value of  $\eta'/\eta$  for  $\eta' = \eta/2$ . The values for  $\tau_C$  and  $\tau_M$  are at most 10% smaller than the values in Table I. These correlation times are in good agreement with earlier results,<sup>1,3,9</sup> and they are enhanced with increasing molecular weight thus showing slower overall motion. However, they do not apply to the whole molecule but to the local framework containing the methyl group. More flexible substituents in larger molecules will have shorter correlation times which is reflected in larger  $T_1$  values. This effect has been used to assign methyl resonances, to simplify a complex spectral region, and to observe conformational changes in cyclic peptides.<sup>16–18</sup> The use of  $\tau_C$  values instead of  $T_1$ , which is not well defined because of the nonexponential relaxation, will give a more precise basis for spectral assignment.

1-Acetylpyrene (1) has a very short correlation time  $\tau_M$  for internal rotation. This methyl group is much more mobile than an ester methyl or one attached directly to a porphyrin or other

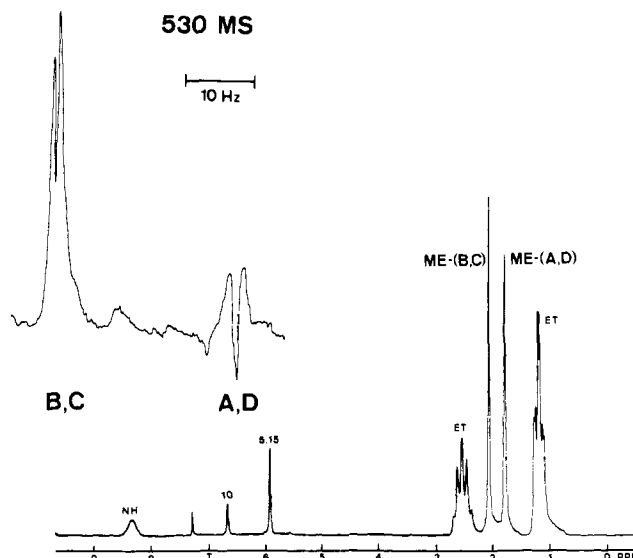


Figure 2. 100-MHz <sup>1</sup>H NMR spectrum of etiobiliverdin (3) in CDCl<sub>3</sub>. The insert shows the methyl resonances near their null point at 0.53 s after the 180° pulse.

Table II. Concentration Dependency of the Chemical Shifts of Compound 2

	concn, mol L <sup>-1</sup>	$\delta$ CH <sub>2</sub> , ppm	$\delta$ CH <sub>3</sub> , ppm
CDCl <sub>3</sub>	0.2	4.21	3.58
	0.4	4.15	3.53
		$\Delta\delta$ 0.06	$\Delta\delta$ 0.05
C <sub>6</sub> D <sub>6</sub>	0.1	3.70	2.95
	0.2	3.70	2.95
		$\Delta\delta$ 0.00	$\Delta\delta$ 0.00

skeleton. We explain this in terms of steric interactions, but further experiments have to be done to clarify this point. The concentration dependence of  $\tau_C$  which characterizes the overall motion of 1 shows no linear correlation with the viscosity of the solution. We therefore conclude that in the more concentrated solution increased stacking slows down the overall motion, thus increasing  $\tau_C$ .

1-Pyrenylacetic acid methyl ester (2) was measured in two different solvents. A quantitative comparison of the correlation times will not seem to be meaningful since they refer to different concentrations too.  $\tau_M$ , however, is not dependent on solvent and concentration as one would expect. The viscosities of both solutions are not very different, whereas the correlation time  $\tau_C$  is doubled in CDCl<sub>3</sub> solution, showing that association occurs at this particular concentration in CDCl<sub>3</sub>. Table II gives the concentration dependence of the chemical shift of the CH<sub>2</sub>- and CH<sub>3</sub>- signal of 2 in both solvents. Both signals exhibit a concentration dependence of the chemical shift in CDCl<sub>3</sub> but not in benzene-*d*<sub>6</sub>, indicating stacking in the chloroform solution.  $\tau_C$  values are therefore a sensitive probe for the study of intermolecular interactions.

Etiobiliverdin (3) has four methyl groups, which are pairwise equivalent, so that only two methyl signals occur in the NMR spectrum (Figure 2). It is known that the molecule is rapidly exchanging between the two helical syn,syn,syn (*Z,Z,Z*) conformations.<sup>19,20</sup> The heterocyclic rings A and D have enhanced mobility which is clearly reflected in the correlation times  $\tau_C$  of the particular methyl groups.  $\tau_C$  of the CH<sub>3</sub> groups attached to rings A and D is 12 ps shorter than  $\tau_C$  of the methyl groups on ring B and C.

Cobester (4) has seven methyl groups; four are propionate methyls, three are acetate methyl groups. Comparing the correlation times for the overall motion one sees that there are

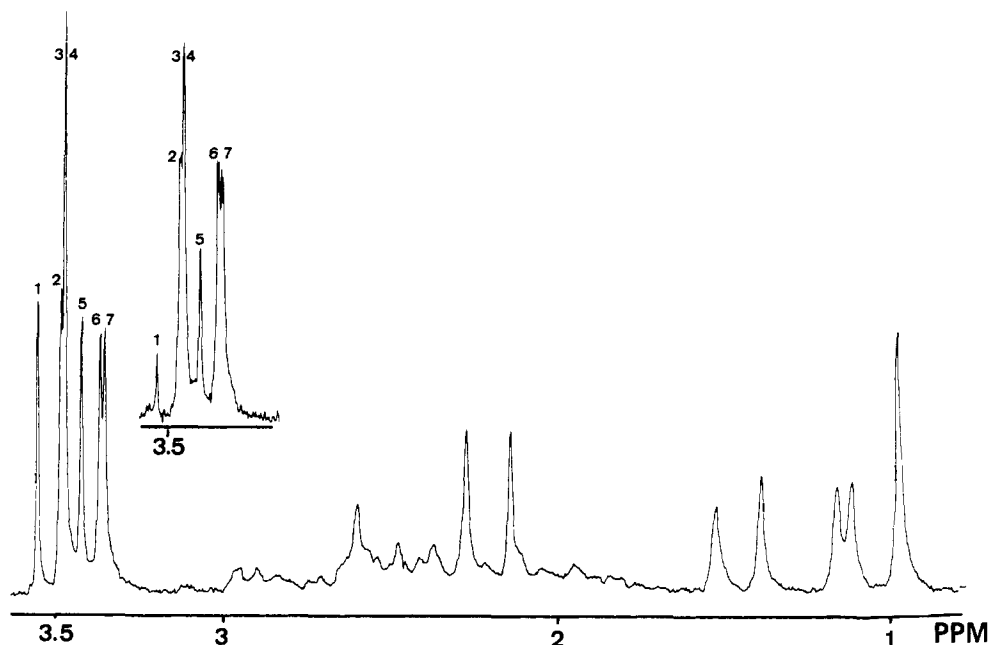


Figure 3. 100-MHz  $^1\text{H}$  NMR spectrum of cobester (4) in benzene- $d_6$  ( $0.02 \text{ mol L}^{-1}$ ). Inserted is the region of the ester methyl groups, 1 s after the  $180^\circ$  pulse, showing still negative components at signals 6 and 7; 2, 6, and 7 are acetate methyl signals and 1, 3, 4, and 5 are assigned to propionate methyls.

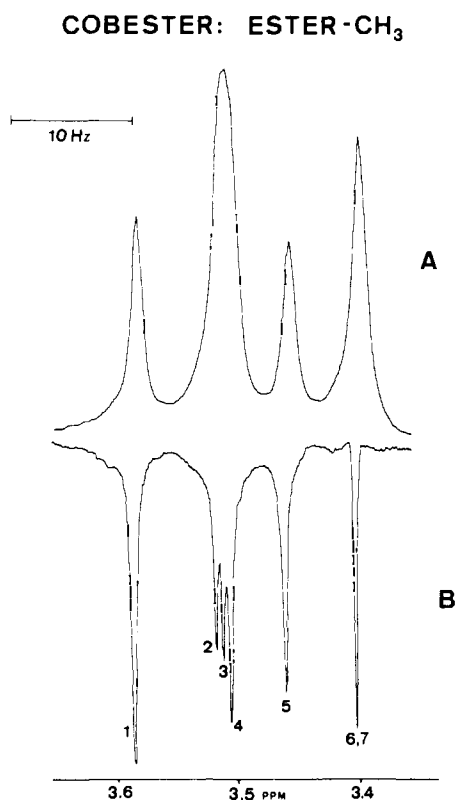


Figure 4. 100-MHz  $^1\text{H}$  NMR spectrum of cobester (4) in benzene- $d_6$  ( $0.05 \text{ mol L}^{-1}$ ): (A) normal spectrum showing overlapping lines; (B) 0.275 s after a  $180^\circ$  pulse. The faster relaxing, broader components have negligible intensity. As only the sharp negative lines remain, small shift differences, which are below the natural line width, can now be observed.

two groups of  $\text{CH}_3$  signals. Three have a  $\tau_C$  value which is longer than 100 ps; four have significantly shorter  $\tau_C$  values. We therefore assign the former to the acetate methyl groups and the latter to the more flexible propionate methyls (Figure 3). No difference signal could be obtained from the methyl groups in the aliphatic region; we attribute this to small long-range couplings obscuring this effect.

Figure 4 shows the spectral region where the ester methyl resonances occur. At this concentration three methyl groups are overlapping. Near the null point of the faster relaxing broader component only the sharp negative signals of the slower relaxing component remain. As their line width is much smaller it is possible to measure shift differences which are smaller than the natural line width.

### Conclusion

Molecular motion can be studied by analyzing the difference signal near the null point of nonexponential relaxing methyl groups. This method is generally applicable to the investigation of internal mobility, association behavior, and solute-solvent interactions of medium or large molecules. As the method depends on observing two coincident signals with different line width, the instrumental resolution must be sufficiently high that the observed line width is mainly determined by  $T_2$ . Unresolved long-range coupling may obscure the differential width of the two peaks. But as the slower relaxing component has usually a much smaller line width, couplings which are smaller than the natural line width might become directly observable when the broader component has no intensity.

**Acknowledgments.** The authors wish to thank Dr. K. P. Wolschann for helpful discussions. The work was supported by Fond zur Forderung der Wissenschaftlichen Forschung in Osterreich No. 3574.

### References and Notes

- (1) H. W. Spiess, *NMR*, **15** (1978), and references therein cited.
- (2) J. W. Harrel, *J. Magn. Reson.*, **15**, 157 (1974).
- (3) J. F. Rodrigues De Maranda and C. W. Hilbers, *J. Magn. Reson.*, **19**, 11 (1975).
- (4) J. D. Cutwell and J. A. Glasel, *J. Am. Chem. Soc.*, **98**, 264 (1976).
- (5) P. S. Hubbard, *J. Chem. Phys.*, **52**, 563 (1970).
- (6) L. G. Werbelow and A. G. Marshall, *J. Magn. Reson.*, **11**, 299 (1973).
- (7) L. G. Werbelow and D. M. Grant, *J. Chem. Phys.*, **63**, 544 (1975).
- (8) G. B. Matson, *J. Chem. Phys.*, **65**, 4147 (1976).
- (9) E. Haslinger and R. M. Lynden-Bell, *J. Magn. Reson.*, **31**, 33 (1978).
- (10) D. R. Whitman, L. Onsager, M. Saunders, and H. E. Dubb, *J. Chem. Phys.*, **32**, 67 (1960).
- (11) R. M. Lynden-Bell and R. K. Harris, "Nuclear Magnetic Resonance Spectroscopy", Th. Nelson and Sons, Ltd., London, 1969.
- (12) R. A. Hoffmann, S. Forsen, and G. Gestblom, *NMR*, **5** (1971).
- (13) A. D. Bain and R. M. Lynden-Bell, *Mol. Phys.*, **30**, 325 (1975).
- (14) W. E. Bachmann and M. Carmack, *J. Am. Chem. Soc.*, **63**, 2494 (1941).

- (15) A. McKillop, B. P. Swann, and E. C. Taylor, *J. Am. Chem. Soc.*, **93**, 4919 (1971).  
 (16) I. S. Dennis, J. K. M. Sanders, and J. C. Waterton, *J. Chem. Soc., Chem. Commun.*, 1049, (1976).  
 (17) E. Haslinger, *Monatsh. Chem.*, **109**, 523 (1978).  
 (18) H. Falk, E. Haslinger, and T. Schlederer, *Monatsh. Chem.*, in press.  
 (19) H. Falk, K. Grubmayr, E. Haslinger, T. Schlederer, and K. Thirring, *Monatsh. Chem.*, **109**, 1451 (1978).  
 (20) W. S. Sheldrick, *J. Chem. Soc., Perkin Trans. 2*, 1457 (1976).  
 (21) F. James and M. Roos, *Comput. Phys. Commun.*, **10**, 343-367 (1975).  
 (22) Equation 12 in ref 9 contains a computation error; all correlation times given there are too long. The correct expression is eq 7 in this paper.

## Quantitative Measurement of Intermediate Species in Sustained Belousov-Zhabotinsky Oscillations

C. Vidal,\* J. C. Roux, and A. Rossi

Contribution from the Centre de Recherche Paul Pascal, Domaine Universitaire, 33405 Talence Cédex, France. Received July 11, 1979

**Abstract:** Sustained Belousov-Zhabotinsky oscillations have been performed in an open continuous-fed reactor, controlled by a computer. A procedure of repeated storage and accumulation of the signal given by any kind of detector allows the identification of several intermediate species and their concentration measurement with a good accuracy. By means of spectrophotometric as well as potentiometric techniques we have so obtained the concentration time dependence of  $\text{Ce}^{3+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Br}_2$ ,  $\text{Br}^-$ , bromomalonic compounds ( $\text{BrMA}$ ),  $\text{O}_2$ , and  $\text{CO}_2$ . These species cannot account for the overall light absorption in the UV range (280–320 nm), so that at least another one, which we could not identify, is involved. A detailed analysis of our experimental results points out for a general agreement with the mechanism already proposed by Field, Körös, and Noyes.

Whereas the oscillatory behavior of the Belousov-Zhabotinsky (BZ) reaction has been studied under various conditions, the oscillating species yet identified experimentally in this system are few. Furthermore, very little is known about the phase differences in the temporal oscillations of these species. Nevertheless, Field, Körös, and Noyes (FKN) proposed some years ago<sup>1</sup> a kinetic model accounting for the temporal and spatial patterns of the BZ reaction. Even if this mechanism appears to be rather successful and its basic assumptions probably valid, no general examination has ever been carried out, owing to the lack of reliable and detailed experimental results. The aim of our work is just such an examination, which in the first place presupposes the collection of a wide set of experimental data.

### I. Experimental Section

**1. Apparatus.** An experimental device, allowing the study of any oscillating reaction in such a way that quantitative and reliable information should become available, has been developed in our laboratory. Since full details appear in previous papers,<sup>2</sup> let us recall only briefly its basic features.

In a continuous-flow stirred tank reactor, fed with reagent solutions at a constant rate, the chemical oscillations can be made highly reproducible. Figure 1 shows, for instance, the high stability of the period reached in a typical experiment on the BZ reaction. Our apparatus, designed to take advantage of this fact, can thus increase as desired the signal to noise ratio of any signal originating in the chemical oscillating system. In short, after each oscillation, the signal given by the detector (spectrophotometer, ion-specific electrode, thermocouple, etc.) is stored and accumulated on a minicomputer (Digital LSI 11). The storage and accumulation procedure is stopped when the accumulated signal is no longer noisy, which is checked on a video terminal. Then the data are transferred to another computer (Digital VAX 11/780) and recorded on its mass memory, so that they are available for subsequent numerical analysis. Each record, 500 points long, covers one and a quarter period.

**2. Experiments.** Two different experiments have been carried out on the BZ reaction with this device. The main difference between them lies in the catalyst chosen,  $\text{Ce}^{3+}$  in the first case and  $\text{Mn}^{2+}$  in the second, for reasons which will become clear later. The reactor volume is 28 cm<sup>3</sup> and mixing is ensured by a glass stirrer rotating at a constant speed of 600 rpm. Other experimental constraints are as given in Table I.

All figures in this paper, excepting Figures 6 and 7, refer to the cerium experiment.

**3. Results.** When the detector in use is a spectrophotometer (Cary 16), the optical density of the reacting medium can be stored at several wavelengths by repeating the procedure described in section II. These different temporal oscillations put together form a matrix, the representation of which is given in Figure 2. We did not try to record the optical density beyond 570 nm because the amplitude of its variation—as well as its absolute value—is too low. On the other hand, below 280 nm the optical density becomes too high (>2) and is no longer measurable. It is quite obvious in Figure 2 that crossing between the stored temporal oscillations and a plane perpendicular to the time axis provides the absorption spectrum of the reacting medium at any given time. An example is displayed in Figure 3, where circles stand for the measured optical density.

In principle the analysis of such a spectrum allows one to determine which species are responsible for the light absorption and to compute the corresponding concentrations. Nevertheless one has to make some assumptions before any calculation can be done. We have divided the field of wavelengths into two parts, assuming that above 320 nm only  $\text{Ce}^{3+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Br}_2$ ,  $\text{HBrO}$ ,  $\text{HBrO}_2$ , and  $\text{BrO}_2^\cdot$  radical<sup>3</sup> are—or might be—encountered. The overall concentration of cerium ions is, of course, time independent, its absolute value being equal to the  $\text{Ce}^{3+}$  inlet concentration. On a first glance at Figure 3, one sees that  $\text{Ce}^{4+}$  is the main absorbing species in this "visible" region. It is unlikely that  $\text{HBrO}_2$  or  $\text{HBrO}$  could be detected when cerium is used as a catalyst: a high concentration of these species would be necessary, because of the great difference between their molar extinction coefficient and the  $\text{Ce}^{4+}$  one. However, cerium ions cannot account by themselves for the overall optical density and at least another species is required. In a first step we tried to fit our results with the set  $\text{Ce}^{3+} + \text{Ce}^{4+}$  and  $\text{BrO}_2^\cdot$ , since the discovery of this radical in the BZ reaction has been recently reported.<sup>4</sup> Unfortunately this attempt failed, least-squares fitting even leading sometimes to negative values of the  $\text{BrO}_2^\cdot$  concentration. On the contrary, when the set  $\text{Ce}^{3+} + \text{Ce}^{4+}$ ,  $\text{Br}_2$  is taken, the fit looks much better. It can still be improved if three independent components are used:  $\text{Ce}^{3+} + \text{Ce}^{4+}$ ,  $\text{Br}_2$ ,  $\text{BrO}_2^\cdot$ . However, the same is also achieved with the set  $\text{Ce}^{3+} + \text{Ce}^{4+}$ ,  $\text{Br}_2$ , continuous absorption at a low level (never more than 0.03 in optical density). In other words, the improvement is insensitive to the shape of the third component spectrum. Hence our results indicate that bromine is an intermediate species in the BZ reaction, whereas they do not allow one to draw any conclusion about the  $\text{BrO}_2^\cdot$  radical.

What happens, now, in the UV region, i.e., between 280 and 320 nm? The contribution of  $\text{Ce}^{3+}$ ,  $\text{Ce}^{4+}$ , and  $\text{Br}_2$  to the optical density is easily computed, since the concentrations of these three species are provided by the previous fit. The experimental light absorption being higher, some other species have to be taken into account. In the range of wavelengths under examination bromate and malonic acid are not