CHEMISTRY LETTERS, pp. 605-606, 1980.

RAPID MEDIUM CHANGE: A NEW METHOD FOR THE DETERMINATION OF BARRIERS TO ROTATION

Mikio NAKAMURA

Department of Chemistry, School of Medicine, Toho University, Omorinishi, Ota-ku, Tokyo 143

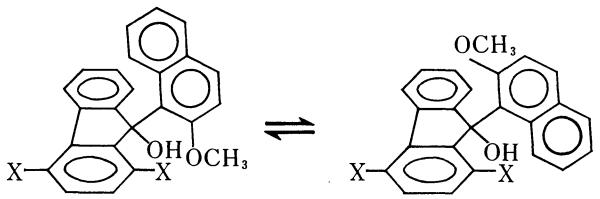
Nobuo NAKAMURA and Michinori ŌKI*

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

A new method for the determination of barriers to rotation, which consists of rapid mixing of a solution with a solvent of different polarity and observing the subsequent relaxation process to a new equilibrium, is developed.

Dynamic NMR has been widely used for the analysis of intra- and intermolecular rate processes[1]. However, this method is not applicable to the cases in which the substrate is thermally labile and yet heating is required for observing the change in line-shape. 1,4-Dimethyl-9-(2-methoxy-1-naphthyl)-fluoren-9-ol (1), mp 159 - 160°C, is one of such examples: heating of its solution in hexachlorobutadiene up to 90°C caused decomposition, whereas the line-shape remained intact.

Since the population ratios, ap/sp, of 1 at 34°C in various solvents changed dramatically, as shown in Table 1, as was 9-(2-methoxy-1-naphthyl)-fluoren-9-ol (2)[2], we expected that it might be possible to follow the population change if the medium was rapidly changed at low enough temperatures. We wish to report the realization of the expectation.



sp *ap*

1 : X=CH_3

2 : X=H

Table 1. Population Ratios (ap/sp) in Various Solvents at 34°C.

Solvent	$CDCl_3$	CCl_4	$(CD_3)_2CO$	$(CD_3)_2SO$
1	0.26	0.64	1.1	5.3
2	0.29	0.71	1.7	8.0

In a typical experiment, 31 mg of 1 was dissolved in 0.20 mL of $CDCl_3$ in an NMR sample tube and the tube was placed in an NMR probe maintained at -50°C. Precooled acetone-d_6 (0.20 mL) was added and the whole solution was mixed thoroughly. The change in signal intensities due to methoxyl protons was followed at 4 points between -0.3°C and 11.4°C, where the rates were conveniently measured. The results are shown in Table 2.[3]

Table 2. Rate Constants for the Isomerization of sp-1 to ap-1 and Equilibrium Constants in $CDCl_3$-$(CD_3)_2CO$ (1 : 1) at Various Temperatures.

Temperature °C	Rate Constant s^{-1}	Equilibrium Constant (ap/sp)
11.4	3.6×10^{-4}	0.54
7.5	1.2×10^{-4}	0.58
3.1	9.6×10^{-5}	0.62
-0.3	6.3×10^{-5}	0.50

The data were put into the Eyring equation and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained as 82.8 $\pm$ 3.3 KJ mol^{-1} and -21 $\pm$ 12 J K^{-1} mol^{-1}, respectively.

Similarly the rates of rotation of the parent compound 2 were obtained as shown in Table 3. Activation parameters were obtained as $\Delta H^{\ddagger}$ = 65.9 $\pm$ 1.0 KJ mol^{-1} and $\Delta S^{\ddagger}$ = -2 $\pm$ 4 J K^{-1} mol^{-1}.

It may be argued that these are the special cases and the method has following drawbacks: 1) since the barrier is obtained in a mixture of polar and nonpolar solvents, both the ground state and the transition state for rotation are complicated, and 2) the barrier thus obtained may be different from that obtained in nonpolar solvents. However, it is also true that a technique for the determination of barrier to rotation of compound 1 is not available at present. Therefore, the method will serve the needs at least until a better technique is developed.

Table 3. Rate Constants for the Isomerization of sp-2 to ap-2 and Equilibrium Constants in $CDCl_3$-$(CD_3)_2CO$ (1 : 1) at Various Temperatures.

Temperature °C	Rate Constant s^{-1}	Equilibrium Constant (ap/sp)
-58.0	4.0×10^{-4}	1.6
-61.0	1.9×10^{-4}	1.5
-65.5	8.4×10^{-5}	1.4
-70.0	4.1×10^{-5}	1.6

Finally we wish to point out that the method should be applicable not only to the case where the substrates are unstable but also to those which the equilibrium constants change widely from one solvent to another and barriers are reasonably high.

References

1) L. M. Jackman and F. A. Cotton, "Dynamic Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York (1975).
2) M. Nakamura, H. Kihara, and M. Ōki, Tetrahedron Lett., 1976, 1207.
3) NMR spectra were obtained on a Hitachi R-20B spectrometer operating at 60 MHz and equipped with a temperature variation accessory.

(Received March 12, 1980)