Application of NMR Spectroscopy of Chiral Association Complexes

12†—Rate Determination of an Intramolecular Motion in a Free Molecule by Means of Dynamic NMR Measurements in the Presence of an Auxiliary Compound‡

Reinhard Küspert§ and Albrecht Mannschreck*
Institut für Organische Chemie, Universität Regensburg, Universitätsstrasse 31, D-8400 Regensburg, FRG

The rate constants of intramolecular processes can sometimes be measured only in the presence of optically active auxiliary compounds. The problem of obtaining the rate for the free molecule was solved by linear extrapolation of rate constant from the complexed to the uncomplexed molecule (LERCUM). This method is developed theoretically and checked experimentally. 2-Bromo-2-methyl-1-(3-bromo-2-methoxy-4,5,6-trimethylphenyl)-1-propanone has the advantage that rotation about its carbonyl-to-aryl bond can be measured both in the presence of (+)-2,2,2-trifluoro-1-phenylethanol as well as in the absence of an auxiliary compound. The novel method of extrapolation is confirmed by the agreement between both results.

INTRODUCTION

Rate constants of enantiomerizations and topomerizations can be made accessible to dynamic NMR by association of the substrate to an optically active auxiliary compound.[3–10] Applications of this method have appeared.[6–9,11–13] An early paper[4] in this series already mentioned the restriction that one cannot be sure whether the measured rate constant is indeed equal to that for the free molecule.

A detailed investigation[6] of one particular system did not detect a significant difference. Although this result encourages further applications, it does not prove that the measured k value will always fit the desired one. Dynamic NMR has also been performed in the presence of achiral lanthanide complexes.[14–21] As far as the influence of the auxiliary upon the results is discussed, this is either done phenomenologically[19] or by determination[21] of all relevant equilibrium constants by methods other than NMR in order to calculate the different rate constants. The effort put into the latter procedure appears to be significant. There are two experimental facts which prohibit determination of the equilibrium constants from the concentration dependence of shifts.[22] (1) It is impossible to perform measurements with an infinite concentration of the auxiliary and rarely possible with a sufficiently large finite concentration. (2) The results are affected by solvation.[23]

This paper presents a method which determines with limited experimental effort a rate constant in a free molecule from measurement in an associated state. The reliability of this method is tested experimentally.

DERIVATION OF THE EXTRAPOLATION METHOD LERCUM

The equilibrium kinetics of a system such as that depicted in Fig. 1 are mathematically solved; this also applies for the most general case,[2] i.e. the two conformations of the free molecule represent diastereoisomers. We shall restrict the discussion, because only the simple cases are of interest for the application.

Assumptions

(i) When assuming the scheme shown in Fig. 1, it is

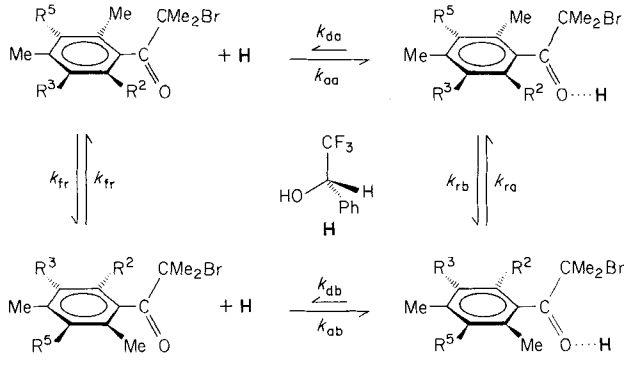

Figure 1. Kinetic model for the processes in solution, demonstrated on highly substituted acetophenones and the auxiliary **H** = (+)-**2**. If the ring is symmetrically substituted (R^2 = Me, $R^3 = R^5$), the rotation around the carbonyl–aryl bond is a topomerization; if not, it is an enantiomerization in the free molecule or a diastereomerization in the association complex, respectively.

* Author to whom correspondence should be addressed.
† For Parts 10 and 11 of the above series, see Ref. 1.
‡ This paper is a contracted part of a thesis.[2]
§ New affiliation: Bruker Analytische Messtechnik, Silberstreifen, D-7512 Rheinstetten 4-Fo., FRG.

CCC-0030-4921/82/0019-0006$03.00

essential that there is only one association complex for each conformation of the substrate or that at least the relative populations of different association complexes do not vary within the concentration range applied. It is questionable whether a lanthanide complex fits this assumption since it offers two places of association. As far as the linearity derived below is experimentally fulfilled, it is probable that the extrapolation can be applied.

(ii) At all usual NMR temperatures, the rates of association and dissociation (Fig. 1) are much higher than the ability of the time resolution of NMR.

(iii) If the intramolecular process of interest in the free molecule represents a topomerization, this is also true for the association complex which means $k_{ra} = k_{rb}$ (Fig. 1). If the process in the free molecule represents an enantiomerization, the corresponding process in the association complex to an optically active auxiliary represents a diastereomerization, i.e. k_{ra} and k_{rb} may differ and, consequently, the two association complexes are unequally populated (Fig. 1). The latter phenomenon has apparently never been experimentally observed; we therefore assume $k_{ra} = k_{rb}$.

Conclusions

Because of (ii), only the conformations of the substrate can be distinguished by NMR, not the free molecule and the association complex corresponding to the same substrate conformation, i.e. the spectrometer separates the system into two 'pots', where pot I corresponds to the upper states in Fig. 1, pot II to the lower ones.

Thus, dynamic NMR monitors transitions

$$\text{pot I} \underset{k}{\overset{k}{\rightleftharpoons}} \text{pot II}$$

where both rate constants are equal because of equal rate constants in the free molecule (Fig. 1) and in the association complex (cf. (iii)).

If Λ is the population of the association complexes, i.e. the molar ratio of association complexes to whole substrate, the known[16] result is

$$k = (1-\Lambda)k_{fr} + \Lambda k_{ra} = k_{fr} + \Lambda(k_{ra} - k_{fr}) \qquad (1)$$

The calculation of the shifts of an individual group in the two pots is also known:

$$\delta_I = (1-\Lambda)\delta_{fr} + \Lambda\delta_a$$
$$\delta_{II} = (1-\Lambda)\delta_{fr} + \Lambda\delta_b$$

where δ_{fr} is the shift of the group in both conformations of the free molecule, δ_a is the shift of the group in the association complex of pot I, and δ_b is the shift of the group in the association complex of pot II. Consequently, the difference of nuclear frequencies of the group in the two pots is given by

$$\Delta\nu = |\delta_I - \delta_{II}|\,\nu_0 = \Lambda\,|\delta_a - \delta_b|\,\nu_0 \qquad (2)$$

where ν_0 is the spectrometer frequency. However, calculation of Λ from Eqn (2) and its insertion into Eqn (1) had apparently not previously been performed. The result is

$$k = k_{fr} + s\cdot\Delta\nu;\ s = \frac{k_{ra} - k_{fr}}{\nu_0\,|\delta_a - \delta_b|} \qquad (3)$$

Therefore, several measurements must be carried out at the same temperature but at differing Λ; the spectra are then evaluated for k and $\Delta\nu$. A plot of k v. $\Delta\nu$ results in a straight line with the intercept k_{fr}. Thus, Eqn (3) serves for the linear extrapolation of rate constant from the complexed to the uncomplexed molecule (LERCUM).

PRACTICAL ASPECTS

Variation of Λ

The values of Λ do not enter the evaluation but it is important that they differ from one another. It will frequently be sufficient to prepare one NMR sample containing a low concentration of auxiliary and to add further unknown amounts of the auxiliary before each subsequent measurement.

Constancy of temperature

Equal temperature for all measurements is decisive but the consequences of small temperature deviations can be corrected in the following way. The expression $k[1-\ln(khk_B^{-1}T^{-1})]\Delta T/T$, derived for constant $\Delta G^{\ddagger}$ from the Eyring[27] equation, is added to k. Another procedure calculates[27] a formal $\Delta G^{\ddagger}$ from the experimental k and T values and uses it for obtaining a corrected k for the desired temperature. It has been shown[2] that further corrections can be neglected.

Evaluation of k and $\Delta\nu$

k and $\Delta\nu$ are obtained by NMR line shape analysis. Some exact methods of evaluation of symmetric uncoupled $A \rightleftharpoons B$ systems have been developed;[26] they take some values directly from the spectrum. More complex spectra are analysed by iteration, e.g. by DNMR5.[25]

Extrapolation of k

The best way of extrapolation is linear regression. However, the program chosen should take into account the individual errors of all k and $\Delta\nu$ values and should also compute the intercept error from them. Apparently, the only program available for this is AUGEDE,[2] based upon a proposal of Deming[28] for the weights of the experimental points.

EXPERIMENTAL

Compounds

2-Bromo-2-methyl-1-(3-bromo-2-methoxy-4,5,6-trimethyl phenyl)-1-propanone (**1**, Fig. 2) (cf. Ref. 8) 6.0 ml (0.12 mol) of Br_2 in 10 ml of $CHCl_3$ are slowly added dropwise to a stirred solution of 11.0 g (0.05 mol) of **3** in 50 ml of $CHCl_3$ at 0 °C; the HBr formed is removed by suction. After 15 h at room temperature and shaking with aqueous Na_2SO_3 the product is worked up with $CHCl_3$ and water. The solvent is removed and the residue is fractionally crystallized in the refrigerator from CH_3OH. The first fractions, m.p. 74–74.5 °C, are purified by sublimation at 80 °C and 0.1 Torr. ^{1}H NMR (CCl_4, 25 °C): $\delta = 1.7$–2.1 (A_3B_3, unresolved coupling; broadening by A/B exchange, maxima at 1.86 and 1.98; $CCH_3^ACH_3^BBr$), 2.22 (s*; 6-CH_3), 2.24 (s*; 5-CH_3), 2.44 (s*; 4-CH_3), 3.62 (s; OCH_3); cf. Fig. 3. Calc. for $C_{14}H_{18}Br_2O_2$ (378.1) 44.47% C, 4.80% H; found 44.35% C, 4.77% H.

2-Methyl-1-(2-methoxy-4,5,6-trimethylphenyl)-1-propanone (3). 22.6 g (0.11 mol) of **4** were *O*-methylated by 2.5 g (0.11 mol) of Na in 130 ml of EtOH and 13.9 g (0.11 mol) of $(CH_3)_2SO_4$; b.p. 89–91 °C, 0.05 Torr: 20.4 g of **3** (81%). ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 1.13$ [d, $J = 7$ Hz; $CH(CH_3)_2$], 2.10 (two s*, unresolved; 5- and 6-CH_3), 2.28 (s*; 4-CH_3), 3.03 [sept, $J = 7$ Hz; $CH(CH_3)_2$], 3.72 (s; OCH_3), 6.53 (s*; H-3'). Calc. for $C_{14}H_{20}O_2$ (220.3) 76.33% C, 9.15% H; found 76.57% C, 8.86% H.

2-Methyl-1-(2-hydroxy-4,5,6-trimethylphenyl)-1-propanone (4) (cf. Ref. 29). 47.7 g (0.35 mol) of 3,4,5-trimethylphenol and 37.3 g (0.35 mol) of isobutyryl chloride are stirred and gently warmed. As soon as the HCl has been evolved, *O*-acylation is finished. For Fries rearrangement resulting in **4**, the ester formed is placed into a funnel connected to a 1 litre three-necked flask which is equipped with stirrer, condenser and drying tube, containing 63.6 g (0.46 mol) of $AlCl_3$, and heated by an oil bath at 90 °C. The ester is added dropwise while stirring. When the formation of foam is reduced the temperature is gradually increased to 140 °C which is maintained for 30 min. After removal of the oil bath, 500 ml of CS_2 are added dropwise while stirring. Addition of 150 ml of concentrated HCl and 300 g of ice dissolves the whole mixture. After work-up with CS_2, steam-distillation of the residue, work-up of the distillate with ether and crystallization in the refrigerator from light petroleum (50–70 °C) yielded several crystalline fractions, the last of which (9.9 g, 14%) had the highest m.p. (86–87 °C). ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 1.13$ [d, $J = 7$ Hz; $CH(CH_3)_2$], 2.07 (s*; 6-CH_3), 2.20 (s*; 5-CH_3), 2.24 (s*; 4-CH_3), 3.25 [sept, $J = 7$ Hz; $CH(CH_3)_2$], 6.54 (s*; H-3', 8.18(s; OH). Calc. for $C_{13}H_{18}O_2$ (206.3) 75.69% C, 8.80% H; found 75.61% C, 8.62% H.

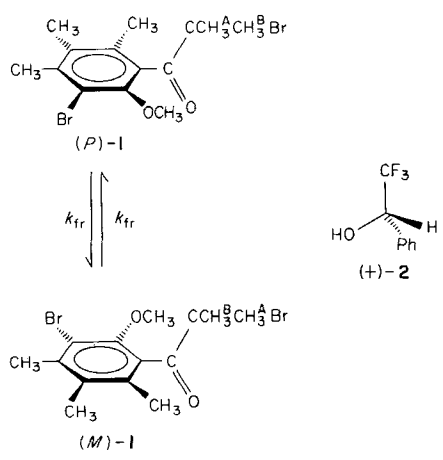

Figure 2. Under conditions similar to those in Fig. 3(a) (+)-**2** generates two different OCH_3 shifts for (*M*) and (*P*),[24] rendering rate determinations possible (including k_{fr} by means of our novel method). In the absence of an optically active auxiliary compound, (*MP*)-**1** shows anisochronous groups CH_3^A and CH_3^B, thereby also rendering a determination of k_{fr} (k_{fr}^* in this special case) possible.

s* Singlet, if couplings between ring methyl groups and benzylic couplings are neglected.

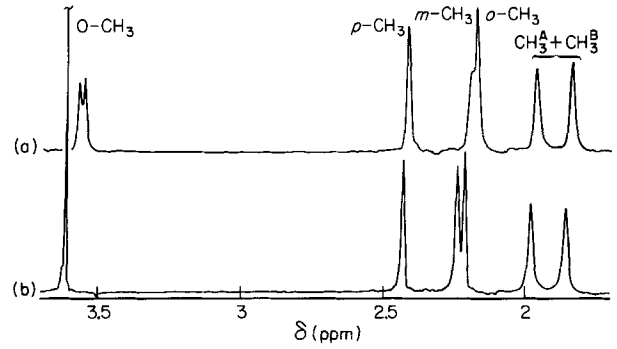

Figure 3. ^{1}H 100 MHz PFT spectra of (*MP*)^{24}-**1** with (a) and without (b) 2.71±0.03 equivalents of (+)-**2** (cf. Fig. 2) in CCl_4 and TMS at 292.7±0.5 K. The assignments[2] of the aryl CH_3 signals are based on their mutual couplings and on incremental values.

(+)-2,2,2-Trifluoro-1-phenylethanol[(+)-2] was bought from Burdick & Jackson Laboratories, Inc., Muskegon, Michigan 49442.

^{1}H NMR Samples

The 5 mm tubes contained solutions in CCl_4 with one drop of TMS per 0.1 ml of solution. For the measurements without auxiliary, (*MP*)^{24}-**1** was 0.25 M, for the measurements with (+)-**2** see Table 1.

^{1}H NMR Spectra

A Varian XL100–15 spectrometer, its V4412 probe and temperature controller, and a 620L–100 computer were used. The control was accomplished via the SYMON module. The temperature was measured by a 'Thermocoax-Miniatur-Mantel-Thermoelement', Chromel-Alumel, external diameter 0.5 mm (Philips GmbH, Kassel, Germany), positioned in an NMR tube in order that it registered the temperature close to the

Table 1. Results of the measurements on (*MP*)^{24}-1 in the presence of (+)-2 in CCl_4 and TMS

v[a]		Molarity of (*MP*)-1	T(K) ±0.5	Δν(Hz)[c] ±0.05	$k_m(s^{-1})$[d] ±0.1	$k_{corr}(s^{-1})$[e] ±0.15
2.71	±0.03	0.260±0.015	293.2	2.37	2.45	2.33
5.47	±0.03	0.235±0.010	292.2	3.07	2.15	2.26
8.80[b]	±0.20	0.230±0.015	292.4	3.77	2.00	2.05
20.50	±0.20	0.146±0.005	292.7	4.33	1.90	1.90

[a] Molar ratio [(+)-2]/[(*MP*)-1]; for smaller v values no measurement is possible because of missing visible splitting (Δν is too small).
[b] cf. Fig. 5.
[c] Nuclear frequency distance of the O-CH_3 signals of (*M*) and (*P*), generated by (+)-2.
[d] Rate constant of (*M*) ⇆ (*P*), evaluated from the spectrum.
[e] Rate constant of (*M*) ⇆ (*P*) at 292.7 K, obtained according to the section on Constancy of temperature.

NMR receiver coil. The temperature was determined before and after each NMR measurement. It was ensured that all parameters influencing temperature remained unchanged. Homogeneity was controlled by the internal ^1H lock signal of TMS; during the measurements the external ^{19}F lock was used. The following parameters were applied: offset 54 kHz; gain 1; spectral amplitude 0.32 to 1.6; one 75° pulse per transient; acquisition time 6 s; delay 1 s; 9–100 transients; spectral width 1024 Hz; data length 12 K; 32 K Fourier data points.

The spectrum of (*MP*)-**1** without auxiliary was recorded at 293.4±0.5 K; the temperatures for the measurements in the presence of (+)-**2** are given in Table 1.

Line shape analyses

In the spectrum without (+)-**2** the absorptions of the CH_3^A and CH_3^B groups (Fig. 2) giving rise to an $A_3B_3 \rightleftarrows B_3A_3$ system were evaluated by trial-and-error simulations using DNMR5.[25] Fig. 4 gives the best fit.

In the spectra (e.g. Fig. 5) with (+)-**2** the absorptions of the OCH_3 groups (Fig. 2) were evaluated. At first, TAPIRS[26] was used which, however, presumes symmetric line shapes, whereas the OCH_3 signals of (*M*) and (*P*) show unequal line widths (0.02 to 0.04 Hz difference). Therefore, a few simulations by

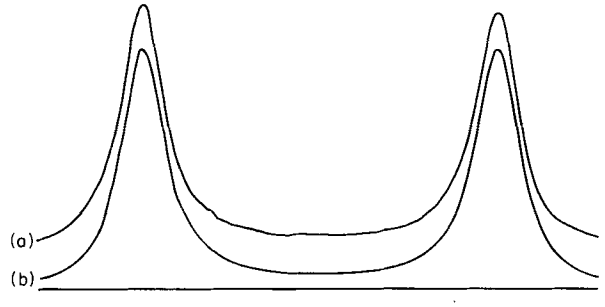

Figure 4. (a) ^1H 100 MHz signal of the geminal Me groups of (*MP*)^{24}-**1** in CCl_4 and TMS at 293.4±0.5 K; $\delta = 1.92$ ppm. (b) DNMR5[25] simulation of an $A_3B_3 \leftrightarrows B_3A_3$ system with $\Delta\nu = 12.5$ Hz, $b_E = 0.72$ Hz, $^4J = 0.25$ Hz, $k = 3.13 \pm 0.25\ s^{-1}$.

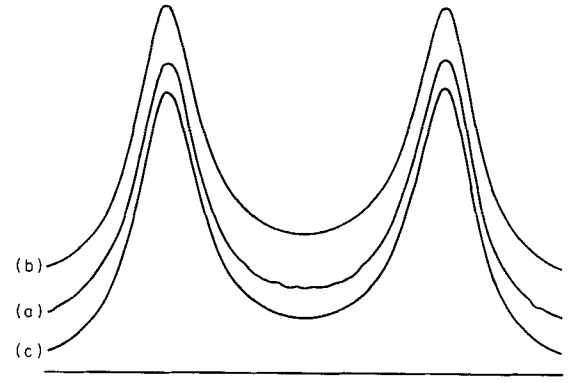

Figure 5. (a) ^1H 100 MHz signal of the OCH_3 groups of (*MP*)^{24}-**1**, 0.23 M, in the presence of 8.8±0.2 equivalents of (+-**2** in CCl_4 and TMS at 292.45±0.5 K; $\delta = 3.48$ and 3.52 ppm. (b) Corresponding TAPIRS[26] fit. TAPIRS is defined for symmetrical line shapes only and produces the following results: $\Delta\nu = 3.78$ Hz, $b_E = 0.42$ Hz, $k = 2.02\ s^{-1}$. The line shape, containing unequal line widths, was to be fitted by subsequent trial-and-error simulations after the TAPIRS procedure. (c) Best fit by means of PLALAB[2] with $\Delta\nu = 3.77$ Hz, b_E(3.52 ppm) = 0.44 Hz, b_E (3.48 ppm) = 0.42 Hz, $k = 2.00\ s^{-1}$.

PLALAB[2] were added which, however, resulted only in minor corrections (cf. Fig. 5). The final k_m and $\Delta\nu$ values are given in Table 1.

Linear extrapolation of the rate constant from the complexed to the uncomplexed molecule (LERCUM)

Since the temperatures of measurement deviated slightly, the k_m values had to be corrected (k_{corr} in Table 1), according to the section on Constancy of temperature, for a common temperature of 292.7 K. The linear regression (Fig. 6) using AUGEDE[2] (cf. Extrapolation of *k*) resulted in $k_{fr} = 2.9 \pm 0.25\ s^{-1}$.

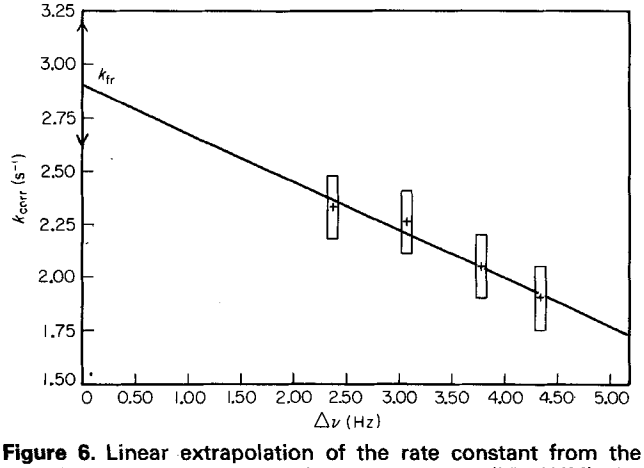

Figure 6. Linear extrapolation of the rate constant from the complexed to the uncomplexed molecule (LERCUM) for (*MP*)^{24}-**1** in the presence of (+)-**2** in CCl_4 and TMS at 292.7±0.5 K. k_{corr}: rate constant of (*M*) ⇆ (*P*) at 292.7 K from Table 1; Δν: nuclear frequency distance of the OCH_3 signals of (*M*) and (*P*), generated by (+)-**2** from Table 1. The linear regression is calculated and plotted by means of the program AUGEDE.[2] The arrows on the k_{corr} axis mark the confidence range of the intercept k_{fr}.

DISCUSSION

The above use of Eqn (3) presumes its coefficient s to be independent of concentration. Indeed, an influence of solvation upon s cannot be excluded. However, an effect of solvation upon the result can probably be neglected, since the dominating interactions such as hydrogen bonds, Lewis-acid/base, and electron-donor/acceptor interactions are taken into account explicitly (cf. the Conclusions section in Derivation of the Extrapolation Method LERCUM). In addition, the concentrations within a series of measurements intended for extrapolation of k will not differ very much. (The ratio between the smallest and largest concentration of auxiliary will not exceed 4.) As a whole, the coefficient s can be assumed to be constant within a LERCUM measurement.

Dynamic NMR in the presence of optically active auxiliaries has been developed for processes which cannot be directly studied in the free molecule. In order to test LERCUM, a molecule was required which also has suitable probes for dynamic NMR of the free molecule. These probes should permit the measurement of the rate of the same process at a common temperature and in a common solvent. Furthermore, the substrate and the auxiliary should conform to Fig. 1 (cf. the Assumptions section (i) in Derivation of the Extrapolation Method LERCUM).

The ketone (*MP*)-**1** and the alcohol (+)-**2** (Fig. 2) fulfil these conditions: rotation about the carbonyl-to-aryl bond in free **1** represents an enantiomerization which exchanges the shifts of $CH_3{}^A$ and $CH_3{}^B$. Therefore, the rate of rotation can be obtained from their absorption. The same process in the association complex with (+)-**2** represents a diastereoisomerization which changes the OCH_3 shift, but does not change it in free **1**. Thus, the exchange between the two 'pots' (see the Conclusions section) can be measured from the OCH_3 absorption.

If indeed LERCUM determines k_{fr}, this value must agree with the one obtained from $CH_3{}^A$ and $CH_3{}^B$ without an auxiliary, i.e. $3.13 \pm 0.25\ s^{-1}$ at 293.4 ± 0.5 K (Fig. 4). (The relatively large error of $\pm 0.25\ s^{-1}$ is due to the strong covariance in the relevant range of line shapes). Since LERCUM (Fig. 6) was carried out for 292.7 K, the above rate constant has to be converted to this temperature (see the section on Constancy of temperature). The result is $k_{fr}{}^* = 2.92 \pm 0.25\ s^{-1}$, obtained without an auxiliary. $k_{fr} = 2.9 \pm 0.25\ s^{-1}$, obtained by LERCUM, is therefore fully confirmed.

Rotation about the carbonyl-to-aryl bond (cf. Fig. 2) in **1** can occur via two diastereomeric transition states. The measured rate constant is, therefore, the sum of two differing elementary rate constants. This fact does not change the applicability of LERCUM to this process. Therefore, the above confirmation is also unchanged.

The negative slope in Fig. 6, together with Eqn (3), shows the rate constant of rotation obtained for free **1** to be larger than the one in its association complex (Fig. 1). The contrary is expected if a stabilization of the transition states by resonance is assumed to be the only reason. Apparently, this electronic effect is overcompensated by additional steric interactions in the transition states.

Computer software

The FORTRAN programs AUGEDE, TAPIRS, and PLALAB can be provided upon request.

Acknowledgements

We are grateful to A. Eiglsperger for the syntheses. Professor H.-D. Lüdemann, Institut für Biophysik und physikalische Biochemie, Universität Regensburg, kindly gave access to the XL100-15 spectrometer. The elementary analyses were performed by Mikroanalytisches Laboratorium, Universität Regensburg. This work was supported by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

REFERENCES

1. Part 11: M. Holík, M. Turečková, A. Mannschreck and G. Stühler, *Org. Magn. Reson.* submitted for publication; Part 10: W. Offermann and A. Mannschreck, *Tetrahedron Lett.* 3227 (1981).
2. R. Küspert, Dissertation, Universität Regensburg (1981).
3. A. Mannschreck, V. Jonas, and B. Kolb, *Angew. Chem.* **85,** 590 (1973); *Angew. Chem. Int. Ed. Engl.* **12,** 583 (1973).
4. A. Mannschreck, V. Jonas and B. Kolb, *Angew. Chem.* **85,** 994 (1973); *Angew. Chem. Int. Ed. Engl.* **12,** 909 (1973).
5. A. Mannschreck, V. Jonas, H.-O. Bödecker, H.-L. Elbe, and G. Köbrich, *Tetrahedron Lett.* 2153 (1974).
6. F. Lefèvre, T. Burgemeister and A. Mannschreck, *Tetrahedron Lett.* 1125 (1977).
7. G. Becher, T. Burgemeister, H.-H. Henschel and A. Mannschreck, *Org. Magn. Reson.* **11,** 481 (1978), and unpublished results.
8. M. Holík and A. Mannschreck, *Org. Magn. Reson.* **12,** 28 (1979).
9. M. Holík and A. Mannschreck, *Org. Magn. Reson.* **12,** 223 (1979).
10. A. Mannschreck, *Nachr. Chem. Tech.* **23,** 295 (1975).
11. A. Tangerman and B. Zwanenburg, *Rec Trav. Chim. Pays-Bas Belg.* **96,** 196 (1977).
12. R. Rauchschwalbe, Dissertation, Universität Regensburg (1977).
13. T. Burgemeister, Dissertation, Universtät Regensburg (1978).
14. H. N. Cheng and H. S. Gutowsky, *J. Am. Chem. Soc.* **94,** 5505 (1972).
15. H. Kessler and M. Molter, *Angew. Chem.* **85,** 1059 (1973); *Angew. Chem. Int. Ed. Engl.* **12,** 1011 (1973).
16. S. R. Tanny, M. Pickering, and C. S. Springer Jr, *J. Am. Chem. Soc.* **95,** 6227 (1973).
17. G. Montaudo, P. Maravigna, S. Caccamese, and V. Librando, *J. Org. Chem.* **39,** 2806 (1974).
18. S. Caccamese, G. Montaudo, A. Recca, F. Fringuelli, and A. Taticchi, *Tetrahedron* **30,** 4129 (1974).
19. H. Kessler and M. Molter, *J. Am. Chem. Soc.* **98,** 5969 (1976).
20. C. V. Krishnan, H. C. Friedman, and C. S. Springer Jr, *Biophys. Chem.* **9,** 23 (1978).
21. H. N. Cheng and H. S. Gutowsky, *J. Phys. Chem.* **84,** 1039 (1980).
22. A. Ejchart and J. Jurczak, *Bull. Acad. Pol. Sci., Sér. Sci. Chim.* **19,** 725 (1971).
23. J. Homer, *J. Magn. Reson.* **34,** 31 (1979), and literature

cited therein.
24. IUPAC, 1974 Recommendations, Section E, Fundamental Stereochemistry, *Pure Appl. Chem.* **45,** 13 (1976).
25. D. S. Stephenson and G. Binsch, *Quantum Chem. Progr. Exch.* **10,** 365 (1978).
26. R. Küspert, *J. Magn. Reson.* accepted for publication; see Ref. 2.
27. H. Eyring, *Chem. Rev.* **17,** 65 (1935).
28. W. E. Deming, *Statistical Adjustment of Data*, p. 178. Wiley, New York (1943).
29. N. Nakamura and M. Ōki, *Bull. Chem. Soc. Jpn* **45,** 2565 (1972).

Received 9 November 1981; accepted 23 November 1981

© Heyden & Son Ltd, 1982