symmetrical ions. The I–Cl bond-length differences here, however, are small compared to the deviations found in the unsymmetrical triiodide ions. As a result, the dichloroiodide group can be considered as a normal anion which is nearly symmetrical. Since there are four anions per cell and only two TAE cationic groups, it follows that the TAE groups are dications.

The structure of the cationic group can be logically discussed in terms of its distortion from a hypothetical planar tetraanisylethylene molecule. Such a molecule could possess three mutually perpendicular twofold axes of rotation. One of these twofold axes lies in the plane of the molecule and is perpendicular to the central double bond. This is the only twofold rotation axis which is conserved in the distortion to the real cation. The projection shown in Figure 1 is along this twofold axis; the idealized planar molecule would have all of its atoms lying along a single straight line in this projection.

The real molecule cannot be planar because of the interaction of the *o*-hydrogen atoms of the phenyl groups. This interaction causes the phenyl groups to twist about the $C_D$–$C_{1A}$ or $C_D$–$C_{1B}$ bonds 28.2° for both ring A and ring B. The phenyl rings are planar; deviations from the best least-squares planes average about 0.02 for each ring. The carbon atom, $C_D$, also lies in the same plane as each of the benzene rings. The oxygen and carbon atoms of the methoxyl groups, however, are displaced slightly from the plane of the phenyl group to which they are attached.

One further distortion from a planar arrangement still exists. In the idealized molecule, carbon atoms $C_D$, $C_{1A}$, and $C_{1B}$ would be coplanar with the equivalent atoms related by the twofold rotation axis, and all six atoms would lie on a straight line in projection—the projection of the $sp^2$ plane of the olefin. In the TAE dication, however, the two groups of atoms are no longer coplanar, but the normals of the two planes make an angle of 41.0° with respect to each other (or 20.5° with respect to the normal of the idealized plane). Since the normals of these planes are in the approximate direction expected for the p orbitals involved in $\pi$ bonding of an olefinic group, one would expect a considerable reduction in the double bond character of the central C–C bond of the molecule. Molecular orbital calculations[10] on tetraphenylethylene give a $\pi$-bond order of 0.685 for the central double bond of the normal molecule and 0.187 for the same bond after the loss of two electrons. Thus, it would appear that, qualitatively, a rather low double bond order is to be expected for this bond in the TAE dication. The bond distance observed for this bond is compatible with this point of view, but, unfortunately, the error in the bond distance is large enough that little significance ought to be placed in it or in the listed value of any of the C–C or C–O bond distances in Table II.

The C–C and C–O distances are reasonably close to the normal values, considering the magnitude of the standard deviations. The average C–C distance in the two benzene rings is 1.392 A for ring A and 1.391 A for ring B. The distances between the atoms of the dichloroiodide group and the atoms of the dication are all greater than 3.5 A, so that normal van der Waals distances appear to exist. The dichloroiodide groups are also well separated from each other (see Figure 2).

## Summary

The crystal structure determination demonstrates the existence of a dicationic species in crystals of TAE-$[ICl_2]_2$. This demonstration makes it seem extremely plausible that the ion also exists in the solvents in which the spectral, nmr, and freezing point studies were made which are reported in a separate paper of this series.

**Acknowledgments.** This research was supported by a National Science Foundation grant (No. GP-3523) for which the authors are very grateful.

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[10] A. Streitwieser, Jr., J. I. Brauman, and C. A. Coulson, "Supplemental Tables of Molecular Orbital Calculations," Vol. II, Pergamon Press, New York, N. Y., 1965, p 1134.

# Nuclear Magnetic Resonance Studies of a Radical–Radical Dimerization Reaction[1]

**David J. Williams and Robert Kreilick**

*Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627.* *Received January 30, 1967*

**Abstract:** We have studied the kinetics of a reaction involving the dissociation of a diamagnetic dimer into two radicals. The reaction may be written as dimer $\rightleftarrows$ 2 radicals. Nuclear magnetic resonance spectroscopy was used to determine rate constants. The equilibrium constant and thermodynamic parameters were determined. A second reaction, involving rearrangement of the dimer, was also studied. The two reactions have the same activation energies but different rate constants.

Nuclear magnetic resonance spectroscopy may be used to study the kinetics of reactions at equilibrium. Characteristic changes in the nmr line shape which occur with composition or with temperature can be used to determine lifetimes and rate constants. Nmr has been used to study the kinetics of numerous types of exchange reactions between diamagnetic materials.[2] These techniques have also been used to

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[1] This work was supported in part by National Science Foundation Grant GP 5482.

study reactions involving exchange between diamagnetic and paramagnetic materials.[3]

We have used magnetic resonance techniques to investigate the kinetics of the dissociation of a diamagnetic dimer into two identical free radicals. The reaction may be written as

$$\mathrm{D} \rightleftarrows 2\mathrm{R} \tag{1}$$

The equilibrium constant for the reaction is given by

$$K = [\mathrm{R}]^2/[\mathrm{D}] \tag{2}$$

The variation between diamagnetic and paramagnetic states broadens the nmr lines of the dimer and allows one to calculate rate constants.

McConnell[3] and Johnson[3] have considered the effect of exchange reactions of this type on nmr line widths. Equations, relating line widths to rate constants, have been derived. The general expression for the contribution of the exchange reaction to the width of a given nmr line is

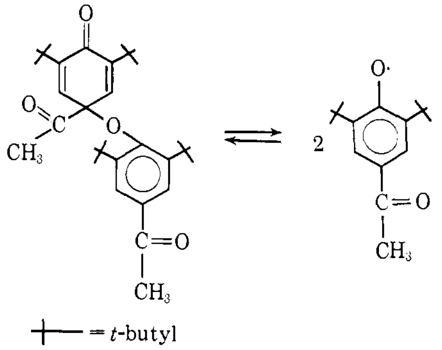
$$(1/T_2) = (1/t_\mathrm{D})\left[\frac{\left(\frac{at}{2}\right)^2}{1 + \left(\frac{at}{2}\right)^2}\right] \tag{3}$$

In this expression, $t_\mathrm{D}$ is the lifetime of the diamagnetic state, $t$ is the lifetime of the paramagnetic state, and $a$ is the electron–nuclei coupling constant of the group of nuclei whose nmr line broadening is being measured. In the limiting case where $(at/2)^2$ is much greater than 1, the equation reduces to

$$(1/T_2) = 1/t_\mathrm{D} \tag{4}$$

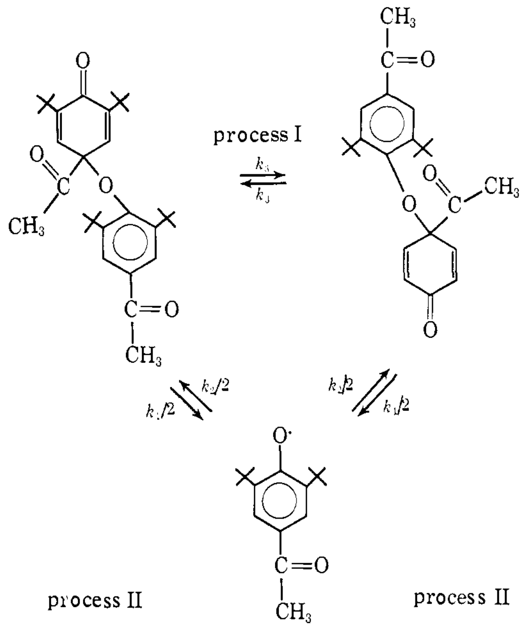
A sufficient condition for the applicability of eq 4 is that the esr spectrum of the paramagnetic species exhibit hyperfine splitting from the group of nuclei whose nmr line broadening is being measured. This condition was fulfilled for our system.

The reaction we have considered is



(5)

All of the nmr lines of the dimer should be broadened equally by this process, if eq 4 is applicable. This behavior is approached at high temperatures (20°). At lower temperatures there is a preferential change in the line shape of the aromatic and quinone ring protons. The behavior observed is characteristic of exchange between two nonequivalent diamagnetic sites. This behavior can be accounted for by a second reaction which interchanges the quinone and aromatic ring protons. A reaction involving an interchange of the two halves of the dimer would produce the observed change in the spectra. The over-all rate process is given by



(6)

Process I involves the interchange of two magnetically different diamagnetic sites. The equations relating nmr line shapes to rate constants, for reactions of this type, are well worked out.[2] In a recent publication,[4] Allerhand and co-workers have discussed the approximations which are normally made in using these equations and have pointed out errors inherent in these approximations.

The rate of both process I and process II should be linearly dependent on the concentration of the dimer, [D]. Rate expressions for the two reactions may be written as shown in (7). In order to calculate the two

process I

$$R_\mathrm{I} = k_2[\mathrm{D}] = [\mathrm{D}]/t_{\mathrm{D}_1} \tag{7a}$$

$k_3 = 1/t_{\mathrm{D}_1}$

$t_{\mathrm{D}_1}$ = dimer lifetime before exchange process I

process II

$$R_\mathrm{II} = k_1[\mathrm{D}] = [\mathrm{D}]/t_{\mathrm{D}_2} \tag{7b}$$

$k_1 = 1/t_{\mathrm{D}_2}$

$t_{\mathrm{D}_2}$ = dimer lifetime before exchange process II

rate constants, one must be able to distinguish between the effect of the two perturbations on the line shape. The acetyl methyl protons on the two halves of the dimer give a single nmr line. This line is affected only by process II, and its broadening can be used to determine $k_1$. The ring and *t*-butyl protons give two lines at low temperatures. These lines can be affected by both process I and process II. In the low-temperature region, process I was found to be dominant, and we were able to determine $k_3$ from changes in the line shape of the ring proton.

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(2) C. S. Johnson, Jr., "Advances in Magnetic Resonance," Vol. I, Academic Press Inc., New York, N. Y., 1965, p 33.

(3) H. M. McConnell and S. B. Berger, *J. Chem. Phys.*, **27**, 230 (1957); C. S. Johnson, Jr., *ibid.*, **39**, 2111 (1963); R. W. Kreilick and S. I. Weissman, *J. Am. Chem. Soc.*, **88**, 2645 (1966).

(4) A. Allerhand, H. S. Gutowsky, J. Jones, and R. A. Meinzer, *ibid.*, **88**, 3185 (1966).

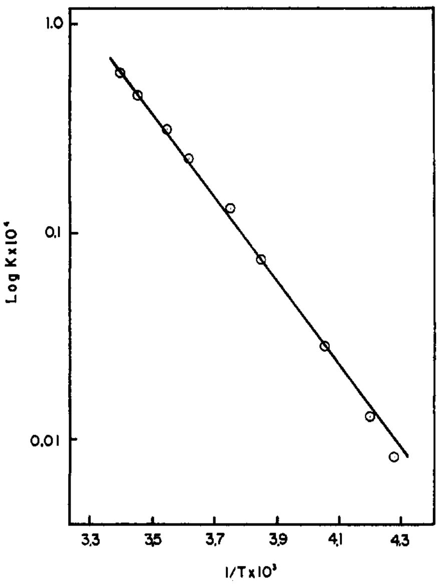

Figure 1. Log equilibrium constant *vs.* $1/T$.

Both of the rate constants and the equilibrium constant are temperature dependent. We have measured the values of the rate constants at a series of temperatures and have calculated activation energies for the two reactions. The temperature dependence of the equilibrium constant was also determined and the standard enthalpy change for the dimerization reaction was calculated.

## Experimental Section

A. **Instruments.** The nmr spectra were taken on a Varian Associates A-60 nmr spectrometer. Esr measurements were made on a JEOLCO 3BSX esr spectrometer. Temperatures were varied by blowing heated or cooled nitrogen gas over the samples. The variable-temperature unit of the A-60 was calibrated with a standard methanol sample. Infrared measurements were made on a Perkin-Elmer Model 421 infrared spectrometer.

B. **Spectra Simulation.** A JEOLCO RA-1 digital computer was programmed with Gutowsky's equation[5] for exchange between two diamagnetic sites. Nmr spectra were calculated with a series of different values of $t_{\mathrm{D1}}$, and a plot of maximum to minimum ratio *vs.* lifetime was made. The separation of the peaks in the absence of exchange was obtained from nmr spectra taken at −60° where the exchange was very slow. We assumed equal populations of the two diamagnetic states, equal lifetimes for the two states, and a natural line width of zero. The plot was used to determine lifetimes from experimental values of the maximum to minimum ratio.

C. **Preparation of the Dimer.** The dimer was prepared by oxidizing 2,6-di-*t*-butyl-4-acetylphenol[6] with $K_3Fe(CN)_6$ in aqueous alkaline methanol.[7] The product precipitated out of solution, as a yellow solid, as the reaction proceeded. The material was filtered and washed with water. The dimer was reasonably stable in the solid state but decomposed quickly in solutions in contact with the air. Attempts were made to recrystallize the dimer, *in vacuo*, from a number of different solvents. Unfortunately, all attempts at recrystallization were unsuccessful. The material was purified by repeated washings, *in vacuo*, with aqueous methanol. We estimate the purity of the dimer to be about 95% on the basis of the area of the nmr peaks.

The structure of the dimer was determined from its nmr and infrared spectra. The nmr spectrum at −60° in $CDCl_3$ has two peaks at $\tau$ 8.90 and 8.77 which can be assigned to the *t*-butyl protons. There is a single acetyl methyl peak at $\tau$ 7.83 and lines from the aromatic and quinone ring protons at $\tau$ 2.52 and 3.88, respectively.

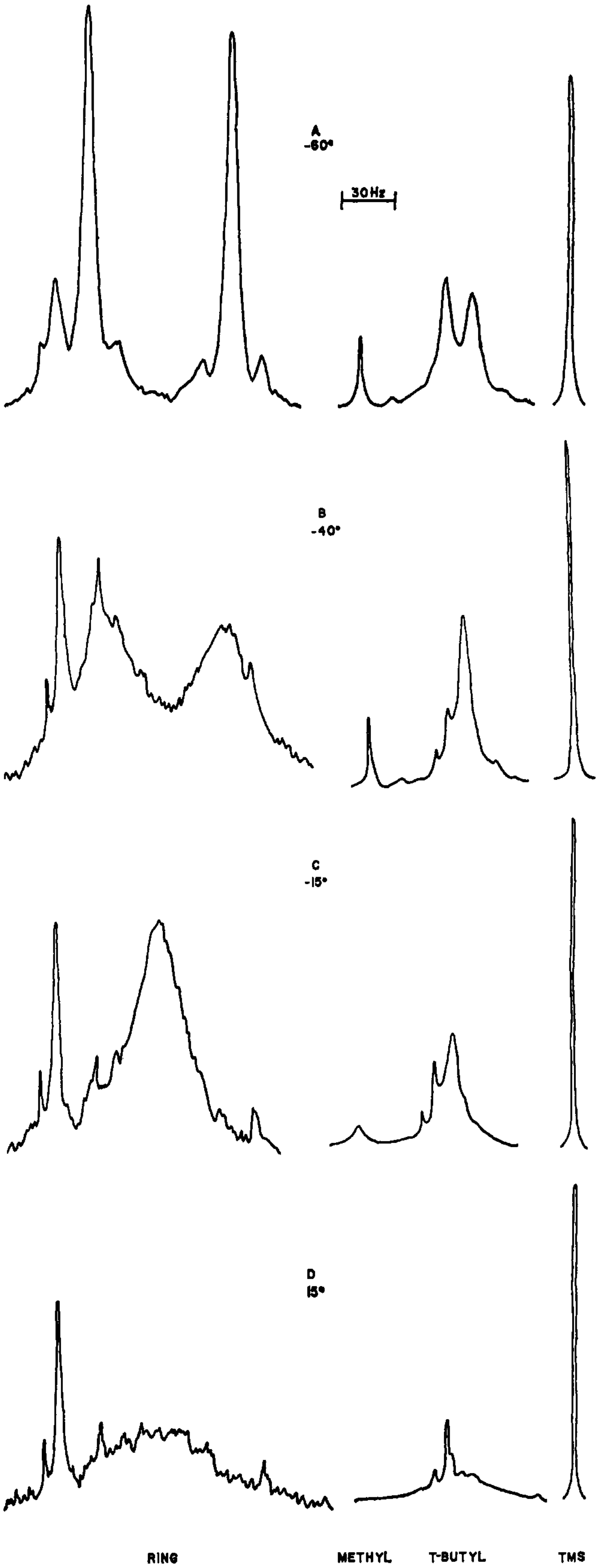

Figure 2. Nmr spectra of the dimer at a series of different temperatures. The spectra were recorded at different gains.

The infrared spectrum of the dimer (Nujol mull) has an intense peak at 1720 cm$^{-1}$ which can be assigned to the unconjugated acetyl carbonyl group. There is a broader peak of about equal intensity at 1660 cm$^{-1}$ which can be assigned to the conjugated acetyl group and/or to the quinone carbonyl. There are also peaks at 1260 and

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[5] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

[6] T. Matsuura, A. Nishinaga, and H. Cahnmann, *J. Org. Chem.*, 27, 3620 (1962).

[7] E. Müller, A. Ricker, R. Mayer, and K. Scheffler, *Ann. Chem.*, **645**, 36 (1961).

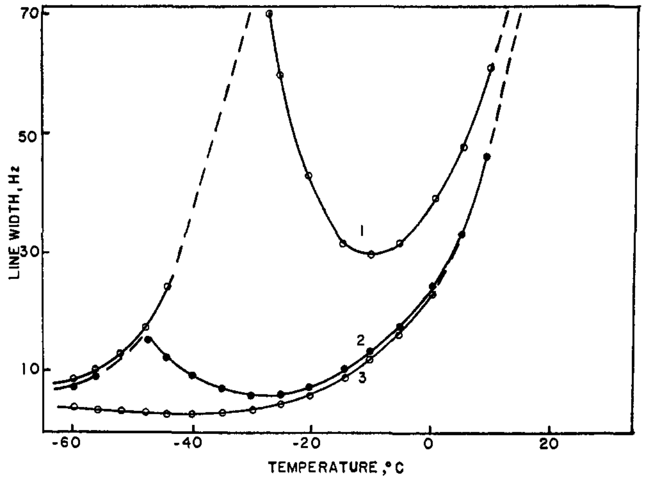

Figure 3. Nmr line width *vs.* temperature: (1) ring protons before and after coalescence; (2) *t*-butyl protons before and after coalescence; (3) acetyl methyl protons.

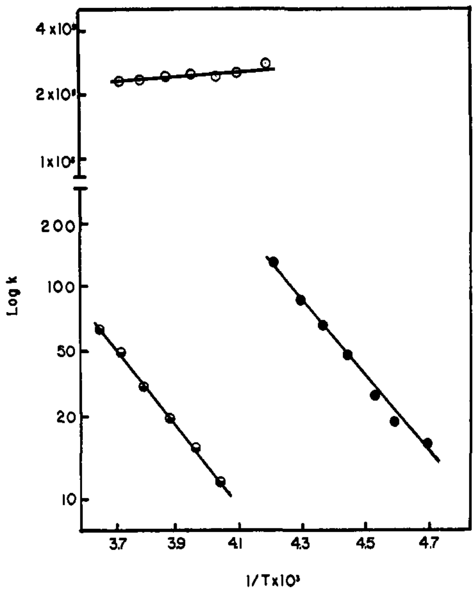

Figure 4. Log *k* *vs.* $1/T$: ◒, $k_1$; ○, $k_2$; ●, $k_3$.

1165 cm$^{-1}$ which can be assigned to carbon–oxygen stretchings in the ether bond.

The esr spectrum of the radical has previously been reported.[8] Splittings from the ring, methyl, and *t*-butyl protons were resolved.

**D. Determination of the Equilibrium Constant.** The equilibrium constant was determined by making dimer solutions of known concentration and measuring the radical concentration by comparing the esr spectra of these solutions with radical solutions of known concentration. The samples were prepared in evacuated, degassed apparatus. Solutions of di-*t*-butyl nitroxide[9] of known concentration were used as standards. The area under the peaks was in each case approximated by the product of the peak intensity times its width squared. Six samples of different dimer concentrations were used and each was compared with three different standard samples. The instrumental conditions were kept as constant as possible during the measurements. Our value of the equilibrium constant at 22° in $CHCl_3$ is $8.8 \times 10^{-4}$ mole/l.

The temperatures of the samples were varied in order to calculate the standard enthalpy change. The radical concentration and equilibrium constant were calculated at each temperature. A plot of log *K* *vs.* $1/T$ is given in Figure 1. Our value for the standard enthalpy change is 9.1 ± 0.5 kcal/mole.

## Results and Discussion

The nmr spectrum of the dimer, at a series of different temperatures, is shown in Figure 2. At −60° both of the reactions are slow and the nmr spectrum is well resolved. The aromatic and quinone ring protons are magnetically nonequivalent and are separated by a chemical shift of 81 Hz. The acetyl methyl protons are magnetically indistinguishable and give a single nmr peak. The line from the *t*-butyl groups on the quinone ring is shifted from the line of the aromatic *t*-butyl groups by 15 Hz. Impurity peaks are present in both the *t*-butyl and aromatic region of the spectrum.

Process I interchanges the magnetic environments of the aromatic and quinone ring protons but should not affect the line from the equivalent acetyl methyl protons. The lines from the *t*-butyl protons are also affected by process I, but because of the small shift between these lines they were not used in our measurements. Process II contributes to the line width of all of the lines in the spectrum. If eq 4 is valid, all of the lines should be broadened equally by this process.

The lines from the aromatic and quinone ring protons are affected by both reactions. At low temperatures both reactions are slow, and one observes sharp lines. As the temperature is raised these lines broaden, move together, and overlap. Finally, the lines collapse into a single broad line which begins to sharpen but then broadens again and finally disappears into the base line. The acetyl methyl protons yield a single sharp line at low temperatures which broadens as the temperature is raised. The line width of this peak is less than that of the lines from the ring protons until one reaches about 10°. Above this temperature this peak is so overlapped with the *t*-butyl peak that accurate measurements are impossible. All of the peaks in the spectrum appear to be approaching the same line widths in this temperature region. A plot showing the change in line widths with temperature is given in Figure 3.

The change in the ring proton lines, in the low-temperature region, is characteristic of exchange between two nonequivalent diamagnetic sites. In this temperature region process I is dominant, and there is only a small contribution from the dissociation reaction. This is evidenced by the small broadening of the acetyl methyl line which is affected only by process II. In this region, one can calculate rate constants for process I from the broadening of the ring lines. The small contribution from process II can be corrected for by assuming that the breadth of the acetyl methyl line is the natural line width. At higher temperature, where the lines have moved together and have started to overlap, one can use maximum to minimum ratios to calculate lifetimes. Broadening from process II is small in this region, and it should not produce very much error in our results.

The rate constant for process II, $k_1$, can be calculated over the entire temperature region from the broadening of the acetyl methyl line. The rate constant for the association reaction, $k_2$, was determined from the values of $k_1$ and the equilibrium constant. Line broadening from the dipolar interaction with the free radical was negligible over the temperature region investigated.

The rates of both process I and process II should show a first-order dependence on the concentration of the dimer. The line broadening should be inde-

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(8) R. W. Kreilick, *J. Am. Chem. Soc.*, **88**, 5284 (1966).

(9) A. K. Hoffmann, A. M. Feldmen, E. Gelblum, and W. G. Hodgson, *ibid.*, **86**, 639 (1964).

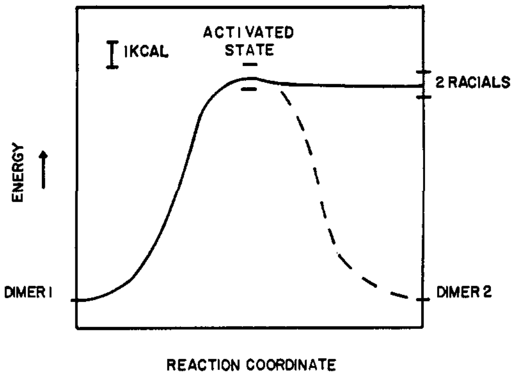

Figure 5. Reaction coordinate *vs.* energy for the two processes.

pendent of concentration in both cases (eq 7). We have conducted experiments in which the dimer concentration was varied incrementally by a factor of 6 (six samples). The line broadening was found to be completely independent of concentration.

A plot of the log of the rate constants *vs.* $1/T$ is given in Figure 4. Data for a series of different concentrations are included in this plot. The rate constant for process I is about a factor of 2 greater than that for process II over the entire temperature region. The two lines are parallel, within experimental error, showing that the activation energies are almost the same.

**Table I.** Rate Constants and Thermodynamic Data at 243°K

| Rate constants and equilibrium constant | Activation energies and standard enthalpy change |
|---|---|
| $k_1 = 7.6 \pm 0.8\ \text{sec}^{-1}$ | $\Delta H_1 = 9.1 \pm 0.5$ kcal/mole |
| $k_2 = (2.5 \pm 0.05) \times 10^5\ M^{-1}\ \text{sec}^{-1}$ | $\Delta H_2^{\ddagger} < 1$ kcal/mole |
| $k_3 = (2.0 \pm 0.1) \times 10^2\ \text{sec}^{-1}$ | $\Delta H_3^{\ddagger} = 9.1 \pm 0.5$ kcal/mole |
| $K = (3.1 \pm 1.0) \times 10^{-5}\ M$ | $\Delta H^{\circ} = 9.1 \pm 0.5$ kcal/mole |

The equivalence of the activation energies might have been anticipated, as the same carbon–oxygen bond is being broken in both reactions. The difference in rates is apparently due to either differences in preexponential factors and/or activation entropies. A plot of the reaction coordinate *vs.* energy, for both reactions, is given in Figure 5. The value of the standard enthalpy change for the dissociation reaction is identical with that of the activation energy within experimental error. Thermodynamic data and rate constants are given in Table I.

## Conclusions

It has been possible to determine rate constants for the dissociation of a dimer into two free radicals with nmr techniques. A second reaction involving rearrangement of the two halves of the dimer was also observed and rate constants were determined. The two processes were found to have the same activation energies but different rate constants.

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# Studies of Chemical Exchange by Nuclear Magnetic Resonance. II. Hindered Rotation in Amides and Thioamides[1]

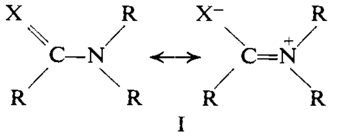
**Robert C. Neuman, Jr., David N. Roark,[2] and Violet Jonas**

*Contribution from the Department of Chemistry, University of California, Riverside, California 92502.*

*Received February 11, 1967*

**Abstract:** A detailed kinetic study of rotation about the central carbon-nitrogen bond in N,N-dimethylcarbamoyl chloride (DMCC) and N,N-dimethylthiocarbamoyl chloride (DMTCC) using *total* nmr line-shape analyses has been carried out. Comparative rotational barriers for amides and analogous thioamides are discussed and the literature is reviewed. Results for DMCC are compared with other available data for this amide and discussed in the light of recent controversy about the significance of chemical exchange studies by nmr. Temperature and concentration dependences of the nmr spectra of DMTCC in carbon tetrachloride indicate significant association of DMTCC into polymeric aggregates. Activation parameters obtained in this study are: DMCC (neat), $E_a = 16.9 \pm 0.5$ kcal/mole, $\log A = 12.9 \pm 0.4$, $\Delta F^*_{298.2} = 16.8$ kcal/mole; DMCC (10.4 mole % in $CCl_4$), $E_a = 17.7 \pm 0.9$ kcal/mole, $\log A = 13.8 \pm 0.7$, $\Delta F^*_{298.2} = 16.3$ kcal/mole; DMTCC ($CCl_4$ solvent), $\Delta F^*_{298.2} \simeq 19$ kcal/mole.

Electron delocalization in amides (I, X = O) and thioamides (I, X = S) causes the rotational barrier about the central C–N bond to be significantly higher



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than that for a normal single C–N bond.[1,3–5] Comparative nmr studies have indicated that these rotational barriers are consistently higher for the thioamides, and this is not unexpected.[1a,5–8]

Interconversion rates of geometrical isomers of unsymmetrically N,N-disubstituted amides[7,9] and thio-

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[1] (a) Part I: R. C. Neuman, Jr., and L. B. Young, *J. Phys. Chem.*, **69**, 2570 (1965). (b) Support by the U. S. Public Health Service (National Institute of General Medical Sciences) through Grant GM-13342 is gratefully acknowledged.

[2] National Science Foundation Undergraduate Research Participant, academic year 1965–1966 and summer 1966.

(3) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 281.

(4) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(5) A. Lowenstein, A. Melera, P. Rigny, and W. Walter, *J. Phys. Chem.*, **68**, 1597 (1964).

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(8) W. Walter, G. Maerten, and H. Rose, *Ann. Chem.*, **691**, 25 (1966).