

# Gas-Phase Kinetics of *N*-Substituted Diacetamide

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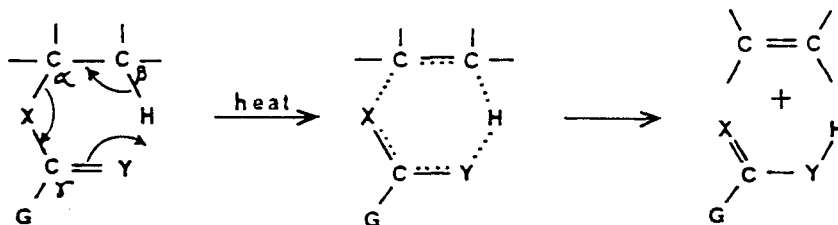
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## Abstract

Gas-phase elimination reactions of number of *N*-substituted diacetamides have been studied. The rates of *N*-phenyl, 4-methoxyphenyl, 4-nitrophenyl, and benzyl diacetamide have been measured between 643–683, 642–693, 673–725, and 555–610 K, respectively. They undergo unimolecular first-order elimination reactions, for which  $\log A = 12.8, 12.9, 12.8$ , and  $11.0 \text{ s}^{-1}$  and  $E_a = 185.7, 191.4, 193.4$ , and  $143.6 \text{ kJ mol}^{-1}$ , respectively. The reactivity of these compounds has been compared with the unsubstituted diacetamide at 600 K. The kinetic data reveals that each of the *N*-aryldiacetamides is less reactive than the parent molecule. We attribute this observation to the resonance of the lone pair of electrons on the nitrogen with either the two carbonyl oxygen atoms or with the  $6\pi$  electrons in the aromatic ring which will result in the stabilization of the *N*-aryldiacetamides related to the parent molecules. © 1994 John Wiley & Sons, Inc.

## Introduction

Our investigation [1] on the rate of thermal decomposition of amides and diamides systems has shown that they involve a 6-membered transition state described generally in eq. (1).



The effect of changing X from O (ester) to NH (amide) has been assessed for simple tert-butyl systems [2,3]. The effect of changing Y from O (amide) to S (thioamide) has been recently described [1]. The substituent effect at the  $C_\alpha$  in simple amide system has been recently investigated and only the effect of methyl group at the nitrogen atom in diacetamide has been analyzed [4]. The pyrolysis of a number of *N*-alkyl-*N*-methylacetamides has been reported to give the corresponding olefins and has required somewhat higher temperature than the pyrolysis of the alkyl acetates [5].

The present work is an investigation on the substituent effect on the nitrogen atom in diacetamide.

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## Experimental

### Synthesis

Refluxing of aniline, 4-methoxyaniline, 4-nitroaniline, or benzylamine with acetyl chloride in a ratio of 1:2 in the presence of pyridine for 2 h gave after normal work-up and fractional distillation, the required compounds as follows:

*N*-phenyldiacetamide: (bp 96–97°C at 0.5 mm Hg), in 72% yield,  $\delta(\text{CDCl}_3)$ , 2.3 (6H, s,  $(\text{COCH}_3)_2$ ), and 7.2–7.5 (5H, m,  $\text{C}_6\text{H}_5$ ) (Found: C, 67.8; H, 6.1; N, 8.0. Calc. for  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$ : C, 67.8; H, 6.2; N, 7.9%).

*N*-(4-methoxyphenyl)diacetamide: (bp 120°C at 0.5 mm Hg), in 70% yield,  $\delta(\text{CDCl}_3)$ , 2.3 (6H, s,  $(\text{COCH}_3)_2$ ), and 3.8 (3H, s,  $\text{OCH}_3$ ) and 7.0 (4H, d,  $\text{C}_6\text{H}_4$ ) (Found: C, 63.8; H, 6.3; N, 6.9. Calc. for  $\text{C}_{11}\text{H}_{13}\text{O}_3\text{N}$ : C, 63.8; H, 6.3; N, 6.8%).

*N*-(4-nitrophenyl)diacetamide: (mp 129°C) from a mixture of petroleum ether 60–80 and benzene in 62% yield,  $\delta(\text{CDCl}_3)$ , 2.3 (6H, s,  $(\text{COCH}_3)_2$ ), 7.7 (2H, d,  $\text{C}_6\text{H}_4$ ) and 8.4 (2H, d,  $\text{C}_6\text{H}_4$ ) (Found: C, 54.2; H, 4.6; N, 12.6. Calc. for  $\text{C}_{10}\text{H}_9\text{O}_4\text{N}_2$ : C, 54.1; H, 4.5; N, 12.6%).

*N*-benzyldiacetamide: (bp 120°C at 0.75 mm Hg), in 75% yield,  $\delta(\text{CDCl}_3)$ , 2.3 (6H, s,  $(\text{COCH}_3)_2$ ), 5.0 (2H, s,  $\text{PhCH}_2$ ), and 7.3 (4H, m,  $\text{C}_6\text{H}_4$ ) (Found: C, 69.2; H, 6.6; N, 7.4. Calc. for  $\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}$ : C, 69.1; H, 6.8; N, 7.3%).

### Kinetic Studies

The flow system used for measuring reaction rates consists of two main parts: CDS custom made pyrolysis unit where the reaction takes place, coupled to a Varian 3300 gas chromatograph, equipped with a  $2\text{m} \times 1/8$  OD, 15% SE30 column on Chromosorb W., AW mesh size 80–100. The pyrolysis unit consists of an insulated aluminum block, a glass reactor vessel, a platinum resistance thermometer, and a thermocouple connected to a Comark microprocessor thermometer. The internal surface of the reaction vessel has been deactivated by injecting 4–5 portions of 50  $\mu$  of allylbromide at 450°C in the absence of air, this process has coated the internal surface of the tube by homogeneous carbon film [6]. The residence time of the sample vapor in the glass reaction is 40–43 s.

### Product Analysis

Solutions of substrates in chlorobenzene were passed down a reactor column packed with helices [6]. The column was heated to temperature comparable to those used in kinetic investigations. The product of pyrolysis were swept out using a stream of nitrogen gas, and the effluents were collected in cold traps. The product obtained from the pyrolysis of *N*-substituted diacetamide were *N*-substituted acetamide and ketene (confirmed by n.m.r. and i.r. spectroscopy) [1].

## Results and Discussion

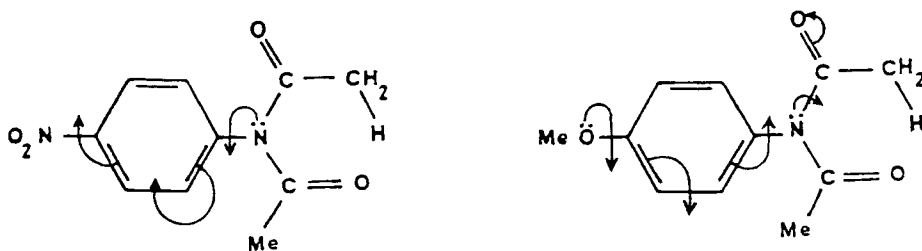
Table I summarizes the first-order rate coefficients of the gas-phase pyrolytic reactions of *N*-phenyl, 4-methoxyphenyl, 4-nitrophenyl, and benzyldiacetamide. Each rate coefficient represents an average of three kinetic runs, in agreement to within  $\pm 2\%$  rate spread. The kinetic runs showed no adverse reactor-surface effects, the

TABLE I. Rate coefficients  $10^3 k(s)^{-1}$  for  $GN(COMe)_2$  pyrolyses.

| G = | Phenyl      |                            | 4-Methoxyphenyl |                            | 4-Nitrophenyl |                            | Benzyl      |                            |
|-----|-------------|----------------------------|-----------------|----------------------------|---------------|----------------------------|-------------|----------------------------|
|     | <i>T</i> /K | <i>k</i> (s) <sup>-1</sup> | <i>T</i> /K     | <i>k</i> (s) <sup>-1</sup> | <i>T</i> /K   | <i>k</i> (s) <sup>-1</sup> | <i>T</i> /K | <i>k</i> (s) <sup>-1</sup> |
|     | 643.6       | 5.1                        | 642.9           | 2.7                        | 673.6         | 5.8                        | 555.6       | 2.9                        |
|     | 653.6       | 8.9                        | 653.7           | 4.5                        | 683.6         | 8.7                        | 565.0       | 4.7                        |
|     | 657.3       | 10.8                       | 678.3           | 16.6                       | 693.9         | 12.9                       | 574.7       | 8.1                        |
|     | 663.4       | 15.0                       | 684.0           | 20.9                       | 703.5         | 20.4                       | 584.8       | 12.9                       |
|     | 673.4       | 25.2                       | 693.8           | 35.5                       | 713.5         | 34.7                       | 595.2       | 20.9                       |
|     | 683.1       | 41.0                       |                 |                            | 720.3         | 45.7                       | 602.4       | 32.4                       |
|     |             |                            |                 |                            | 725.7         | 57.5                       | 609.8       | 46.8                       |

kinetic rate using an empty carbonized reaction vessel was compared with that of similar vessel packed with glass helices, this increase in the surface to volume of approximate nine-fold has not affect the kinetic rate. Since a six-fold change in the amount of substrate used per kinetic run gave no significant change in rate coefficient, these reactions were deemed to be first-order processes. The Arrhenius parameters seem to be in agreement with the pathways proposed for these reactions (Table II).

The kinetic data reveals that each of *N*-aryl substituted diacetamide is less reactive than the diacetamide itself. We attribute this observation to the resonance effect between the aromatic 6- $\pi$  electrons and the unshared pair of electrons on the nitrogen, Scheme I which will result in the stabilization of the *N*-aryldiacetamide relative to the parent molecule.



Scheme I

Since these reactions are facilitated by nucleophilic attack by the carbonyl oxygen upon  $\beta$ -hydrogen, so one would think that a phenyl group, which delocalizes the lone pair of electrons away from the nitrogen, should reduce the rate. This is observed,

TABLE II. Arrhenius parameters and rate data at 600 K for pyrolysis of  $GN(COMe)_2$ .

| G               | $\log A(s)^{-1}$ | $E_a kJmol^{-1}$ | $10^4 k(s)^{-1}$ | $k_{rel}^a$ |
|-----------------|------------------|------------------|------------------|-------------|
| H <sup>b</sup>  | $11.9 \pm 0.4$   | $151.3 \pm 2.7$  | 532.9            | 1           |
| Phenyl          | $12.8 \pm 0.6$   | $185.7 \pm 7.5$  | 4.3              | 124         |
| 4-Methoxyphenyl | $12.9 \pm 0.0$   | $191.4 \pm 0.0$  | 1.7              | 313         |
| 4-Nitrophenyl   | $12.7 \pm 0.3$   | $193.4 \pm 4.9$  | 0.7              | 761         |
| Benzyl          | $11.0 \pm 0.2$   | $143.6 \pm 2.4$  | 314.1            | 2           |

<sup>a</sup>  $k_{rel}$  is the relative rates of diacetamide to *N*-aryldiacetamides.

<sup>b</sup> Literature value [4].

likewise a 4-nitrophenyl group should be more effective in this and should give a bigger rate reduction. This is observed. However, a 4-methoxy group should give an increased rate over phenyl. This is not observed. Moreover, the dramatic increase in rate by introducing a methylene group between the nitrogen and the aromatic ring to form *N*-benzyldiacetamide proves further that the rate suppression effect of the aryl groups on the gas-phase elimination reactions of the diacetamides is a result of resonance stabilization of reactant relative to the unsubstituted diacetamide.

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### Bibliography

- [1] N. A. Al-Awadi, R. F. Al-Bashir, and O. M. El-Dusouqui, *J. Chem. Soc., Perkin Trans. 2*, 579 (1989).
- [2] R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1025 (1975).
- [3] A. Maccoll and S. Nargra, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1108 (1973).
- [4] N. A. Al-Awadi, *J. Chem. Soc., Perkin Trans. 2*, 2187 (1990).
- [5] H. E. Baumgarten, F. A. Bower, R. A. Setterquist, and R. E. Allen, *J. Amer. Chem. Soc.*, **80**, 4588 (1958); W. J. Bailey and C. N. Bird, *J. Org. Chem.*, **23**, 996 (1958).
- [6] C. H. Depuy and R. W. King, *Chem. Rev.*, **60**, 436 (1960).

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