# Kinetic Study of Oxidation of N-(α-Methylbenzylidene) Anilines by Dimethyldioxirane

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ABSTRACT: A kinetic study of the oxidation of substituted N-(α-methylbenzylidene) anilines by dimethyldioxirane was investigated using a UV/VIS spectrophotometer. Oxaziridines and nitrones were formed as intermediates, and in the excess of dimethyldioxirane corresponding carbonyl compounds, nitrosobenzene or nitrobenzene, were formed quantitatively. The kinetic data were used in the equation for the formation of oxaziridines and nitrones as an intermediate and further oxidation to the corresponding acetophenones and nitrosobenzene. Hammett $\rho$ values were determined for compounds *p*-substituted on the aromatic ring attached to the carbon atom of the imino group, and it was found that these substituents have very little effect on the oxidation reaction. © 2007 Wiley Periodicals, Inc. Int J Chem Kinet 39: 492–497, 2007

## INTRODUCTION

Imines as unsaturated compounds can be oxidized by a variety of oxidizing agents. The first step of oxidation usually results in products known as oxaziridines or nitrones. The formation of these two compounds depends very much on the structure of the original imine, the type of oxidizing agent, and the reaction conditions. Oxaziridines are useful as aprotic-oxidizing agents, and nitrones are useful for spin trapping in ESR experiments [1].

In the reaction with *m*-Cl-peroxybenzoic acid, oxaziridines are the main products and nitrones are formed only in a few cases. Nitrones are preferably formed when a carbon atom of an imine group is stericly hindered [2,3]. The formation of nitrones in reactions with peroxyacids was characterized as an abnormal pathway for the reaction and the formation of oxaziridine as normal [4].

Oxaziridines can be prepared by a reaction of imines with molecular oxygen in the presence of transition metal complexes [2]. High yield of oxaziridines from imines was obtained in the oxidation reaction using an adduct of hydrogen peroxide to urea, known as urea–hydrogen peroxide (UHP), in combination with maleic anhydride or other anhydrides. In cases when aryl groups are attached to the nitrogen atom of imino group, nitrones are formed preferably [5]. In the oxidation of imines by permanganate, nitrones are formed [6]. The presented data indicate that water plays a very important role and a cyclic intermediate is predicted.

It was discovered that some oxaziridines can be converted to the corresponding nitrones by a thermal reaction, especially in cases where nitrones are

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thermodynamically more stable than oxaziridines. The oxaziridines can be photochemically converted to nitrones and vice versa—an important path for the preparation of optical pure oxaziridines [7].

The formation of nitrones in the reactions of *C*-aryl-*N*-alkyl imines with dimethyldioxirane was ascribed to the electrophilic nature of this oxidizing agent [3]. Overoxidation of *C*-aryl *N*-alkyl imines by dimethyldioxirane results in aldehydes and nitroalkanes [8].

The majority of the studies have been done with imines, where alkyl or aryl groups were attached to the carbon atom of the imino group and alkyl groups to the nitrogen atom of the imino group. The oxidation of these compounds by dimethyldioxirane formed nitroalkanes and the corresponding carbonyl products.

We did not find experimental data for the oxidation of substituted *N*-(α-methylbenzylidene) anilines to the corresponding oxaziridines and nitrones as intermediates, and further oxidation to carbonyl and nitroso or a nitro compound especially in view of the kinetic study of such an oxidation. To our knowledge, this kind of kinetic data has not been presented so far.

## METHODOLOGY

For our study, we prepared an acetone solution of dimethyldioxirane according to known procedure [8] and substituted *N*-(α-methylbenzylidene) anilines (**1a–g**), as shown in Fig. 1, were prepared according to the literature procedure [9]. The solution of dimethyldioxirane should be dried at least 48 h prior to any use.

The reaction of the oxidation of substituted *N*-(α-methylbenzylidene) anilines (**1a–g**) with a dry solution of dimethyldioxirane in acetone was followed by measuring the absorbance at 750 nm to track the formation and further oxidation of oxaziridine and at 500 nm to track the formation and further oxidation of nitrone in a thermostated cell in a UV–VIS spectrophotometer (Varian Cary 100), within the temperature range of 10–50 ± 0.2°C.

Under experimental conditions, we did not detect any interfering compounds at the wavelengths used. The reaction mixtures were analyzed by GC/MS (Hewlett Packard HP 6890) and $^1$H NMR (Brucker Avance DPX 300). An example of the GC/MS chromatogram—from the reaction of the oxidation of unsubstituted imine—is shown in Fig. 2. We confirmed the formation of oxaziridines (**3a–g**) and nitrones (**4a–g**) as intermediates.

Further oxidation produced carbonyl compounds (**5a–g**) and nitrosobenzene, which was immediately oxidized to nitrobenzene. We could detect the formation of a nitroso compound when no excess of dimethyldioxirane was used. We did not detect any measurable conversion of oxaziridines to nitrones and vice versa, under our experimental conditions. In all

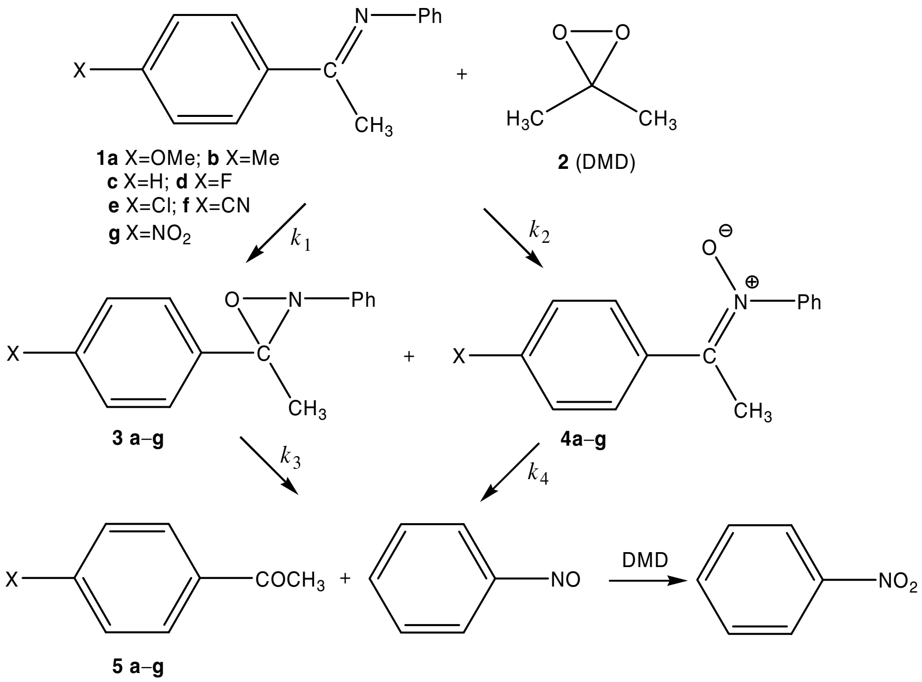

**Figure 1** Reaction scheme.

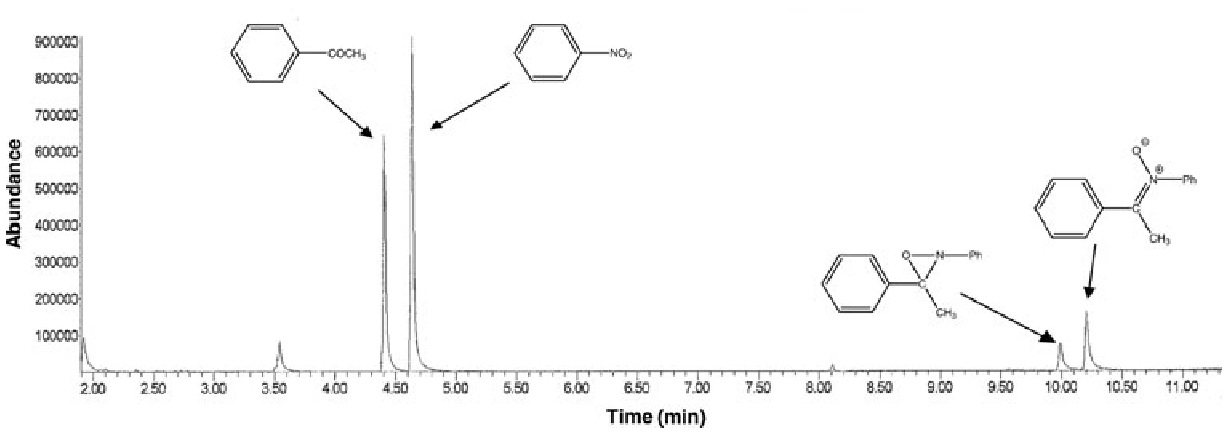

**Figure 2** Typical GC/MS chromatogram of the reaction mixture.

kinetic experiments, dimethyldioxirane was used in 10-fold excess.

The starting concentration of dimethyldioxirane was approximately 0.1 mol/L. The exact concentration of dimethyldioxirane was determined before each kinetic run by oxidation of excess thioanisole (subsequent GC/MS analysis) and was in agreement with that determined using the UV method ($\lambda_{max} \sim 330$ nm and $\varepsilon = 10$).

The kinetic data were used in Eq. (1)

$$Y = \frac{a \cdot b \cdot (\exp(-b \cdot t) - \exp(-c \cdot t))}{c - b} \qquad (1)$$

where $Y$ is the concentration of an intermediate, $t$ is time (s), $a$ is the initial concentration of $N$-($\alpha$-methylbenzylidene) aniline, $b$ is the rate constant for the formation of an intermediate (oxaziridine or nitrone), and $c$ is the rate constant for further oxidation of an intermediate (oxaziridine or nitrone).

For the calculation of Hammett values, the classical Hammett equation has been applied [10] (Eq. (2))

$$\ln\left(\frac{k_{sub}}{k_0}\right) = \sigma \cdot \rho \qquad (2)$$

where $k_{sub}$ represents the rate constant for substituted $N$-($\alpha$-methylbenzylidene) aniline, $k_0$ the rate constant for unsubstituted $N$-($\alpha$-methylbenzylidene) aniline, and $\sigma$ the substituent constant.

## RESULTS AND DISCUSSION

In all reactions, substituted $N$-($\alpha$-methylbenzylidene) anilines, oxaziridines, and nitrones were oxidized as intermediates and were confirmed by $^1$H NMR and GC/MS analysis.

Maximum concentrations of these two compounds, under experimental conditions (at 40°C), were observed for 20 to 30 min. Nitrosobenzene was detected in all cases when dimethyldioxirane and imines (**1a–g**) were used in the ratio 2:1.

Carbonyl compounds (**5a–g**) and nitrobenzene were formed quantitatively (96–98%) in 2 h if a 10-fold excess of dimethyldioxirane was used. The formation of singlet oxygen in these reactions was not detected. We found out that the presence of light did not have a measurable effect on the composition of reaction products.

**Table I** Second-Order Rate Constants for the Oxidation of Substituted N-($\alpha$-Methylbenzylidene) Anilines at 40°C

| | Oxaziridines | | Nitrones | |
|---|---|---|---|---|
| X | $k_1$* (L mol$^{-1}$s$^{-1}$) | $k_3$* ($10^{-2}$ L mol$^{-1}$s$^{-1}$) | $k_2$* (L mol$^{-1}$s$^{-1}$) | $k_4$* ($10^{-2}$ L mol$^{-1}$s$^{-1}$) |
| a | 0.392 ± 0.025 | 7.30 ± 0.35 | 0.72 ± 0.05 | 2.93 ± 0.15 |
| b | 0.500 ± 0.015 | 6.45 ± 0.45 | 0.68 ± 0.03 | 2.88 ± 0.12 |
| c | 0.518 ± 0.020 | 6.59 ± 0.23 | 1.02 ± 0.05 | 2.37 ± 0.10 |
| d | 0.458 ± 0.028 | 7.04 ± 0.50 | 1.11 ± 0.04 | 2.03 ± 0.05 |
| e | 0.547 ± 0.031 | 8.22 ± 0.43 | 1.21 ± 0.05 | 2.39 ± 0.10 |
| f | 0.749 ± 0.042 | 9.22 ± 0.55 | 2.35 ± 0.03 | 1.33 ± 0.12 |
| g | – | – | 2.05 ± 0.04 | 0.89 ± 0.05 |

*$r^2 = 0.93$–$0.97$.

**Table II** Second-Order Rate Constants for the Oxidation of Unsubstituted N-($\alpha$-Methylbenzylidenne) Aniline

| | Oxaziridines | | Nitrones | |
|---|---|---|---|---|
| $T$ (K) | $k_1$* (L mol$^{-1}$s$^{-1}$) | $k_3$* ($10^{-2}$ L mol$^{-1}$s$^{-1}$) | $k_2$* (L mol$^{-1}$s$^{-1}$) | $k_4$* ($10^{-2}$ L mol$^{-1}$s$^{-1}$) |
| 283 | 0.385 ± 0.020 | 1.69 ± 0.05 | | – |
| 288 | 0.455 ± 0.022 | 1.89 ± 0.05 | – | 0.28 ± 0.01 |
| 293 | 0.494 ± 0.020 | 2.15 ± 0.08 | – | 0.49 ± 0.02 |
| 303 | 0.520 ± 0.030 | 3.33 ± 0.03 | 0.45 ± 0.01 | 1.38 ± 0.02 |
| 308 | 0.572 ± 0.025 | 4.87 ± 0.10 | 0.80 ± 0.01 | 1.67 ± 0.03 |
| 313 | 0.596 ± 0.040 | 6.08 ± 0.10 | 1.02 ± 0.03 | 2.37 ± 0.02 |
| 323 | 0.708 ± 0.025 | 7.07 ± 0.25 | – | 2.69 ± 0.02 |

*$r^2 = 0.93$–$0.97$.

We determined the second-order rate constants for the first-step oxidation to oxaziridines (**3a–g**) and nitrones (**4a–g**) and further oxidation to the corresponding carbonyl compounds (**5a–g**) and nitrobenzene. The second-order rate constants obtained from UV/VIS, under pseudo-first-order conditions at 40°C, are presented in Table I. The rate constants are an average of at least two determinations. In all cases, good to excellent correlation was found, and experimental error was estimated at ±5%.

Using the Arrhenius method, we determined the activation energy ($E_a$) for the unsubstituted $N$-($\alpha$-methylbenzylidenne) aniline. For the formation of oxaziridine, it was 5.2 ± 0.15 kcal/mol and for further oxidation of oxaziridine it was 7.2 ± 0.15 kcal/mol; and for the formation of nitrone, we were not able to determine the activation energy, but for further oxidation of nitrone the activation energy was 12.5 ± 0.20 kcal/mol. The second-order rate constants are presented in Table II.

**Table III** Hammett $\rho$ Values at 40°C

| | Oxaziridines | | Nitrones | |
|---|---|---|---|---|
| | $k_1$* | $k_3$* | $k_2$* | $k_4$* |
| Hammett $\rho$ | 0.24 | 0.09 | 0.49 | −0.34 |

*$r^2 = 0.91$–$0.94$.

A Hammett plot (Fig. 3) of the second-order rate constants, for the first step oxidation, toward oxaziridines and nitrones and for the second step of oxidation of oxaziridines and nitrones, to carbonyl compounds and nitrosobenzene, shows fair to good linear free energy relationship (LFER) against $\sigma$ constants ($r^2 = 0.91$–$0.94$).

The Hammett $\rho$ values are presented in Table III. An example of UV/VIS kinetic data of substituted $N$-($\alpha$-methylbenzylidene) anilines oxidation (**1a–g**) is presented in Fig. 4.

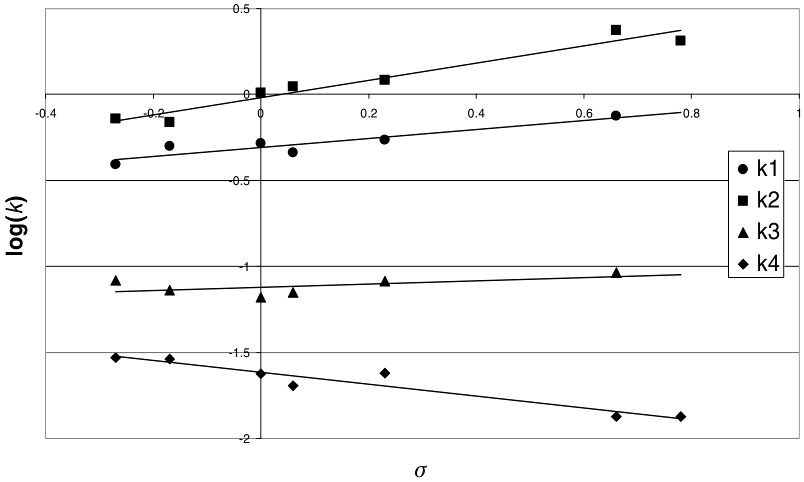

**Figure 3** Hammett plot of the second-order rate constants.

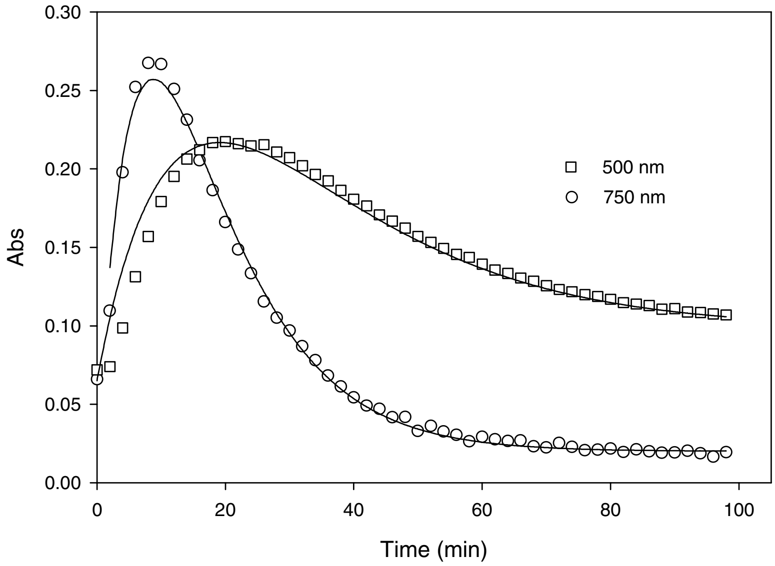

**Figure 4** UV/VIS kinetic data at 750 and 500 nm at 25°C for the oxidation of unsubstituted *N*-(*α*-methylbenzylidene) aniline by dimethyldioxirane.

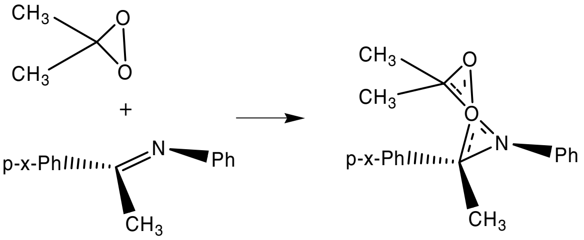

**Figure 5** Suggested formation of the spiro transition state.

## CONCLUSIONS

*N*-(*α*-Methylbenzylidene) anilines substituted at the *p* position of the aromatic ring attached to the carbon atom of an imino group were prepared. The oxidation of the substituted *N*-(*α*-methylbenzylidene) anilines (**1a–g**) by dimethyldioxirane was investigated.

Oxaziridines (**3a–g**) and nitrones (**4a–g**) were formed as intermediates. They are very sensitive to further oxidation to the corresponding acetophenones (**5a–g**) and nitroso or nitrobenzene.

The magnitude of Hammett *ρ* values shows that electron-withdrawing groups and electron-releasing group, at the *p* position of aromatic ring attached to the carbon atom of the imino group, have very little effect on the oxidation reaction. The influence of substituents on the aromatic ring attached to the nitrogen atom of imino group is under investigation.

The value of Arrhenius activation energy for the first step of oxidation of unsubstituted *N*-(*α*-methylbenzylidene) aniline is in agreement with the literature data for the epoxidation of simple olefins by dimethyldioxirane, where Baumstark and McCloskey suggested the spiro transition state [11] and Bach et al. also proposed in their calculations the spiro transition state [12].

We believe that the first step of oxidation of *N*-(*α*-methylbenzylidene) anilines, substituted on the aromatic ring attached to the carbon atom of imino group, occurs through a spiro transition state (Fig. 5).

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