same ratio. In experiments with excess vinyl halide, the unreacted vinyl halide was partially isomerized at the end of the reaction.

Reactions in 80% Ethanol. Reaction of 0.0435 mol/l. of *cis*- or *trans*-bromide in 0.39 *N* sodium hydroxide in 80% ethanol (7 ml) at 120° was followed titrimetrically. The half-life is about 45 min, and products were determined after 24 hr. After evaporation of the solvent, extraction with carbon tetrachloride, drying and concentrating, nmr showed the formation of the ketone **8** and ether **9** in a 3:1 ratio. Crystallization of the oil (methanol) gave a solid (10 mg, 15%) which depressed the mixture melting point with **8**, showed in the ir no sign for **1**, **2**, or **8**, and had C=C absorption at 1610 cm⁻¹. It was tentatively assigned as the ether **9**. On standing, the ketone **8** (30 mg, 50%) was separated and identified by ir, nmr, and mixture melting point.

The reactions of the vinyl halides (0.0435 mol/l.) and *p*-toluenethiolate and benzylthiolate ions (0.087 mol/l.) were conducted in ampoules at 120° At the end of the reaction the solvent was evaporated, the residue dissolved in carbon tetrachloride and washed with 5% sodium hydroxide, but traces of the free thiol were, however, always present. Analysis of the product by nmr was discussed.

Reactions in Dimethylformamide. In reactions in dimethylformamide the solvent was evaporated at the end of the reaction, the oil dissolved in carbon tetrachloride, washed with water, and the organic layer dried and evaporated.

Reaction of **1** (90 mg, 0.3 mmol) in dimethylformamide (20 ml) for 80 hr at reflux showed that 10% of **1** still remained. The only product formed was the ketone **8** (nmr). In dimethylformamide containing 3% water, **1** disappeared completely after 40 hr.

Reaction of **2** (90 mg, 0.3 mmol) in dimethylformamide (20 ml) gave after 31 and 40 hr, 24 and 30%, respectively, of **1**, while 64

and 70% of **2** were formed from **1** after 22.5 and 30 hr. The accompanying product was **8**.

Reactions with Lithium Chloride. Quantitative separation between the chlorides and the bromides by vpc or tlc were unsuccessful. The disappearance of the bromide was therefore followed by the ir peaks at 575 (for the *cis*), 615 (for the *trans*) and 960 cm⁻¹ (for both bromides). The formation of the chloride was followed by the 635 cm⁻¹ peak of the *trans*-chloride and the 970 cm⁻¹ peak which is common to both chlorides. The chloride–bromide ratio was determined from the intensities of the 960 and 970 cm⁻¹ peaks. The 575 cm⁻¹ peak is common for both the *cis* chloride and bromide and additional quantitative determination was by integration of the methoxy signals in the nmr. The error in the combination of the method may be as high as 10%.

a. Lithium chloride (750 mg, 18 mmol) and **1** (350 mg, 0.89 mmol) were refluxed in dimethylformamide (70 ml) for 136 hr. The oil showed formation of a 1:1 ratio of chlorides and was crystallized from methanol. A solid, mp 120–121° (40 mg, 13%), was precipitated and identified as *trans*-chloride **11d** by analysis, ir, and mixture melting point. After few hours, another fraction (20 mg, 6.5%) was precipitated and shown by ir to be a 6:4 ratio of **10d** to **11d**. No attempt was made to isolate more material.

b. Lithium chloride (435 mg, 10.5 mmol) and **2** (200 mg, 0.5 mmol) were refluxed in dimethylformamide (50 ml) for 136 hr. The oil contained a 1:1 ratio of chlorides and crystallized from methanol. On a few days standing pure **11d**, mp 120–121° (25 mg, 14%), was obtained and identified by ir and mixture melting point.

c. Lithium chloride (23 mg, 0.55 mmol) and **1** (120 mg, 0.3 mmol) were refluxed in acetic acid (7 ml) containing sodium acetate (6 mg, 0.08 mmol) at 120.3° for 280 min. The ir showed the formation of 50% chlorides which were in a 1:1 ratio of *cis* to *trans* and the remaining 50% bromides were in a 4:6 ratio of *cis* to *trans*.

Meisenheimer-Type Compounds from Heteroaromatic Substrates. The Reaction of Methoxide Ion with 3,5-Dinitro-4-methoxypyridine in Methanol Solution[1]

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Abstract: The formation and isolation of sodium 4-aza-1,1-dimethoxy-2,6-dinitrocyclohexadienate (adduct III) as resulting from the action of CH₃ONa on 3,5-dinitro-4-methoxypyridine in methanol solution are described. The structure of the adduct was proved by spectral evidence (nmr, uv and visible, and ir). The equilibrium constant and the rate of formation have been determined and compared with similar data for the trinitro analog I. The implications of the present results on the influence of aza activation on the mechanism of nucleophilic aromatic substitution are discussed.

In recent studies on nucleophilic heteroaromatic substitution[2] the physical organic aspects of aza activation have been contrasted with those of nitro activation. In several instances the effect of the aza group on reactivity is similar to that of the nitro group; but relevant differences also exist, such as the lower steric requirements of the aza group and its relatively important H-bonding interactions with the medium.[3] With regard to the reaction mechanism, a two-stage process *via* the formation of an intermediate σ complex is well established in the case of nitro activated aromatics.[4] A main piece of evidence in support of this hypothesis is the actual detection and isolation of the Meisenheimer compounds,[5] *i.e.*, the adducts formed from picryl ethers and alkoxides. In recent years, typical Meisenheimer compounds, such as I, have been intensively investigated in view of their theoretical importance as reaction intermediates; the subject has been reviewed recently.[6,7]

(1) Nucleophilic Heteroaromatic Substitution. XXXI.

(2) G. Illuminati, *Advan. Heteroc. Chem.*, 3, 285 (1964).

(3) G. Illuminati, G. Marino, and G. Sleiter, *J. Amer. Chem. Soc.*, 89, 3510 (1967); F. Genel, G. Illuminati, and G. Marino, *ibid.*, 89, 3516 (1967); M. Calligaris, G. Illuminati, and G. Marino, *ibid.*, 89, 3518 (1967).

(4) J. F. Bunnett, *Quart. Rev.* (London), 12, 1 (1958); S. D. Ross, *Progr. Phys. Org. Chem.*, 1, 31 (1963).

(5) In this and subsequent papers of the series the terms "Meisenheimer compound" and "adduct" are referred, for convenience, to the cyclohexadienate ion derivative, *i.e.*, to the anionic part of the Meisenheimer-like salt.

(6) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, 16, 61 (1966).

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It has been pointed out[2] that similar information is needed in the case of aza-activated substrates, although the well known adducts of pyridine with alkyl metals[8] do belong to the same class of compounds. For this reason we have become interested for some time in the elucidation of the following main points: (1) to what an extent an aza group, as incorporated in a heteroaromatic system, promotes the formation of an adduct by reaction with MeO^- and other familiar nucleophiles; (2) what is the structure of the adducts; (3) what is the role of the adduct formation in nucleophilic heteroaromatic substitution.

An obvious starting point in this program is methoxy-s-triazine, which is the aza analog of 2,4,6-trinitroanisole, the precursor of Meisenheimer compound I. According to preliminary studies in this laboratory, isolation, or even detection, of an adduct of type II have not proven to be so straightforward as in the case of complex I.


I   II
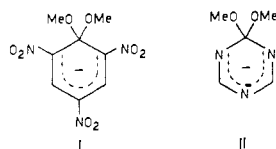
While triazine derivatives are still the object of our current interest, it also seemed worthwhile to approach our problem by considering heteroaromatic structures deriving from the gradual replacement of nitro with aza groups. This proved to be a useful approach, since we have obtained clean cut evidence for the formation of adducts by the replacement of a single nitro group with an aza group starting from 2,4,6-trinitroanisole.

Following a recent preliminary report,[9] we now wish to describe in detail the structure and the modes of formation of the compound formed by the interaction of methoxide ion with 3,5-dinitro-4-methoxypyridine. Because of its decidedly different behavior, the reaction of the 2-methoxy isomer will be dealt with in the subsequent paper.

Results and Discussion

Adduct Formation. (a) Isolation and Structure. 3,5-Dinitro-4-methoxypyridine and methoxide ion form a 1:1 adduct, which can be isolated as an orange solid from a concentrated methanol solution.

The nmr spectrum of the adduct was recorded in both methanol and DMSO-d_6 as solvents. In the latter solvent it consists of two singlets, at τ 1.22 and 7.08, whose intensity ratio is 1:3. An identical signal, τ 1.40, in the low-field region, is obtained in methanol solution. The starting 3,5-dinitro-4-methoxypyridine shows two singlets at τ 0.68 and 5.91; in this case the intensity ratio is, as expected, 2:3. The observed pattern for the adduct is consistent with structure III, the low-field signal being assigned to the equivalent ring protons, and the high-field signal to the six equivalent methoxyl protons.
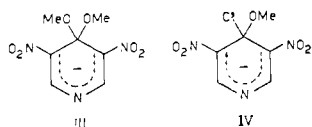
III   IV

Structure III is further supported by comparison with the Meisenheimer compound I. The structure of this compound is a well established one by several independent methods; recently, the X-ray structure has also been worked out.[10] The nmr spectrum[11] is analogous to the one now observed for the adduct of 3,5-dinitro-4-methoxypyridine (Table I).

Table I. Summary of Spectral Data for Adducts I and III

Spectral method	I	III
Nmr, τ, ppm,[a] ring		
protons, methoxyl group	1.36	1.22
protons	6.97	7.08
Uv and visible, λ_{max},	$414 (2.6 \times 10^4)$	$308 (4.9 \times 10^3)$
mμ (ϵ_{max})[b]	$487 (1.8 \times 10^4)$	$455 (1.8 \times 10^4)$
Ir, ν, cm^{-1}; relative	1206; vs	1195; vs
intensity[c]	1161; s	1167; s
		1143; vs
	1124; m	1121; s
	1096; vw	1088; w
	1063; s	1060; s
	1045; s	1020; s

[a] Values relative to TMS (τ = 10.00). Measurements in DMSO solution (DMSO-d_6, when necessary). The data for I are found in ref 11. [b] Measurements in methanol solution. The data for I are from R. Foster and R. K. Mackie, J. Chem. Soc., 3796 (1963). [c] Measurements in Nujol mull in the ketal region (± 1 cm^{-1}). The data for I are from ref 13.

Electronic and vibrational spectral behavior is also in agreement with a Meisenheimer-type structure. Thus, on going from 3,5-dinitro-4-methoxypyridine to the 1:1 adduct a strong band appears in the visible region at 455 mμ (ϵ_{max} 1.8 $\times$ 10^4), and the characteristic bands for ketals[12] are observed in the ir region from 1040 to 1225 cm^{-1}. These spectral features are also similar to those of adduct I and related compounds[13–15] (Table I).

On the base of the spectral properties, our results show that adduct III appears to be identical with that recently obtained by Dyall and his coworkers[16] upon the reaction of the methoxide ion with 4-chloro-3,5-dinitropyridine and that it can indeed be formed by the direct action of the methoxide ion on the parent 4-methoxypyridine compound and not necessarily by solvolysis of adduct IV.[17]

(b) Equilibrium Constant. The formation of adduct III in methanol solution has been ascertained to be a reversible reaction. Starting from a solution of the pyridine compound at a given concentration, on addition of a sufficient excess of the methoxide reagent, the equilibrium can be shifted completely toward adduct formation and the intensity of the absorption band reaches a maximum value from which the extinction coefficient was calculated. From the optical density at

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(17) Contrary to a misprint in the summary of their paper, Dickeson, et al. (see ref 16), did not obtain the adduct from the parent 4-methoxypyridine derivative because, for some reason, they actually failed to prepare such a compound.

Table II. Equilibrium Constants[a] for the Formation of Adducts I and III in Methanol at 25°

[MeO⁻], M	—[2,4,6-Trinitroanisole] = 3.58 × 10⁻⁵ M—			—[3,5-Dinitro-4-methoxypyridine] = 3.45 × 10⁻⁵ M—			K_1/K_{III}
	OD_{410}	α	$K_1 \times 10^{-3}$, M^{-1}	OD_{455}	α	$K_{III} \times 10^{-3}$, M^{-1}	
3.95×10^{-2}	0.895	1.000		0.609	1.000		
7.90×10^{-4}	0.842	0.941	21.0	0.414	0.680	2.77	7.6
3.95×10^{-4}	0.750	0.838	14.2	0.275	0.452	2.18	6.5
1.975×10^{-4}	0.569	0.636	10.0	0.159	0.261	1.87	5.4

[a] The mean deviation from the mean was 3.7% as based on duplicated experiments.

455 mμ the equilibrium constant for the formation of this adduct in methanol solution was determined at 25°.

The equilibrium constant for adduct I has been determined by several authors.[18] Since the agreement between the published values is only fair and we were mostly interested in relative stabilities, we have determined the K values for both adducts I and III under identical conditions. It should be emphasized that the equilibrium constant for III has never been obtained starting from the parent 4-methoxypyridine derivative.[17] The K values are reported in Table II. They are found to decrease with decreasing concentrations of the reagent, in agreement with the observations by Bernasconi[22] on the adduct of 2,4-dinitroanisole. The change also affects the K_I/K_{III} ratio (Table II) to some extent.

Despite the above-mentioned uncertainties, the results show that the replacement of nitro by an aza group located *para* to the geminal position causes a decrease in stability of the adduct. This effect is interpreted in terms of more effective delocalization of the electronic charge in the nitro group. The stability difference is not very large and this may be partly due to the compensating effect of solvation since an aza group is found to be more subject to specific solvation than a nitro group in hydroxylic solvents.[3,23]

It is of interest to note that possibly because of the lack of steric influences a nitro group *para* to the geminal position plays a major role in determining the stability of the Meisenheimer adduct. Thus, the charge of the anion appears to be especially concentrated on this group for adduct I.[24] In support of this view, the recent work by Fendler, *et al.*,[19] shows that the replacement of the nitro group by a cyano group causes a much greater decrease of the stability of the adduct at the *para* than at the *ortho* position. At the *para* position the influence of the aza group on the stability of the adduct turns out to be intermediate between that of the nitro and the cyano groups.

(c) Reaction Rate. The formation of the Meisenheimer compound I from 2,4,6-trinitroanisole is sufficiently slow to permit rate measurements by standard methods.[14,25] Rate measurements were also carried out for the pyridine analog by following the spectral

change at 455 mμ, with an excess of the methoxide reagent under pseudo-first-order conditions. Because of the relatively high reactivity of this substrate, it was found convenient to run the kinetic experiments at 20°. For the sake of comparison we ran similar measurements for the formation of adduct I at the same temperature. The rate constant, k_1, for the reversible reaction

$$\text{substrate} + \text{MeO}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{adduct}$$
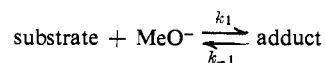
was calculated from the equation $k_{obsd} = k_1(b + K^{-1})$, k_{obsd} being the observed pseudo-first-order rate constant, K the equilibrium constant, and b the methoxide ion concentration. The k_1 and k_{-1} values are reported in Table III.

Table III. Rate Constants for the Formation and Decomposition of Adducts I and III in Methanol at 20°

MeO⁻, 10^4 M	2,4,6-Trinitroanisole (TNA)			3,5-Dinitro-4-methoxypyridine (DNMP)		
	TNA, 10^5 M	k_1[a]	$k_{-1} \times 10^3$ [b]	DNMP, 10^5 M	k_1[a]	$k_{-1} \times 10^3$ [b]
3.58	3.78	7.04[c]	0.51	5.28	9.7[c]	5.0
7.15	3.78	7.17[c]	0.48	5.28	11.6[c]	4.7
7.71	4.22	9.50		5.82	12.4[c]	4.2
9.64	4.22	9.70		5.82	12.9	4.1
14.3	3.78	10.26[c]		5.28	13.8[c]	4.1
19.3	4.22	10.26[d]		5.82	14.1[c]	3.6
35.8	3.78	10.33[c]		5.28	13.4	4.0

[a] (M^{-1} sec⁻¹); the mean deviation from the mean, as based on duplicate runs, was 3.4% for TNA and 2.3% for DNMP. [b] (Sec⁻¹); calculated from $k_{-1} = k_1/K$, from values of K measured at 20°, when available. [c] Run in duplicate. [d] Run in triplicate.

It is thus found that the rates of the forward and reverse reaction for the formation of adduct III are both greater than the corresponding values for the formation of adduct I. The lower stability of the former adduct (see Table II) derives from the especially large increase of the rate of the reverse reaction, the forward reaction rate being only about 1.4 as great as that of the latter adduct.

In the reaction of 2,4-6-trinitroanisole with ethoxide ion in ethanol solution, the formation of the Meisenheimer compound is accompanied by a different kind of interaction, which is fast and reversible but not necessarily part of a multistep process. Such an interaction has been assumed to be of no relevant influence on k_1 in the formation of adduct I in methanol solution.[25] In the present work no evidence for the formation of any complex prior to (and other than) adduct III was obtained in similar conditions. Thus, the above rate comparison (between k_1 values) is likely to reflect the true state of affairs.

(18) The most reliable values are probably those determined by Gold and Rochester[14] and by Fendler, *et al.*,[19] who report 7700 and 17,000, respectively, at 25°. A lower value by Abe, *et al.*,[20] has been questioned by Murto, *et al.*,[21] and by Dickeson, *et al.*[18]

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Implications on the Mechanism of Nucleophilic Heteroaromatic Substitution. The replacement of a nitro group with an aza group at the position *para* to the reactive center results in a decrease in the stability of the Meisenheimer compound and in an increase in its rate of formation. The differences are small but indicate a trend which may have a bearing on the mechanism of nucleophilic heteroaromatic substitution. To the extent the assumption of a two-step mechanism involving a Meisenheimer-type compound as a true reactive intermediate is a valid one, a possible combination of these effects on the potential energy *vs.* reaction coordinate diagram may lead to a flattening in the two-peak profile (Figure 1, dotted line). The change is toward a one-step mechanism but is probably too small to warrant a change in mechanism. Furthermore, considering the small influence of the replacement of a nitro group by a cyano group at a position *ortho* to the methoxy group of 2,4,6-trinitroanisole,[19] *a fortiori* the replacement by an *ortho*-aza group should not affect the stability of the Meisenheimer adduct to any appreciable extent. We ought to conclude that adduct II should not be much less stable than adduct III. However, the experienced difficulties in obtaining adduct II (see introductory part) stimulates further work to collect direct evidence with triaza substrates.

A final remark must be made in connection with the possibility that the formation of adduct III might be preceded by attack of the reagent on a hydrogen-bearing nuclear position. This phenomenon is now a well-established one starting from 2,4,6-trinitroanisole and related compounds.[19,26] A similar attack is observed with 3,5-dinitro-4-methoxypyridine in DMSO-d_6 solution. On addition of either sodium or potassium methoxide a characteristic peak for a 1,3-adduct was observed in the nmr spectrum ($\tau = 3.98$). The spectrum slowly changes over that of a mixture probably containing some 1,1-adduct, three peaks being observed in the region $\tau = 1.5$. A more thorough study of the occurrence of adducts of this kind with aza-activated substrates (2-methoxy isomer) is reported in the following paper.

Experimental Section

Materials. Methanol (reagent grade) was dried by refluxing and distilling over magnesium; during these operations the distillation column was protected from atmospheric CO_2 and moisture. For concentrations from 0.1 M up to about 5 M, stock sodium methoxide solutions were directly prepared by dissolving freshly cut metallic sodium into methanol, under a nitrogen atmosphere. The most concentrated (nearly 5 M) solution was obtained when no more metal could be dissolved without external heating. Such solutions were titrated with 0.1 N H_2SO_4, a mixture of bromocresol green and methyl red being the indicator. Less concentrated solutions were obtained by adding solvent to a 0.1 M solution. Commercial (Merck) deuterated dimethyl sulfoxide, DMSO-d_6, was used as such (minimum deuteration, 99%). 2,4,6-Trinitroanisole was prepared by the nitration of anisole at 80° and purified by recrystallization of the product to constant melting point, 68.5–70.0°, lit.[27] 68.0–69.0°.

3,5-Dinitro-4-methoxypyridine. 4-Chloro-3,5-dinitropyridine was prepared with the method described by Signor.[28] To a solution of 1.0 g of this compound (5.26×10^{-3} mol) in the least amount of anhydrous methanol 1 equiv of a sodium methoxide solution was added dropwise under magnetic stirring, at 40–50°. After 1 hr,
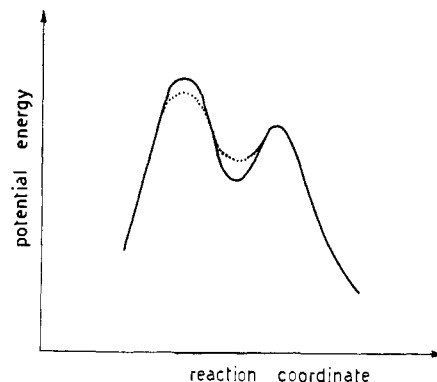
Figure 1. *Possible* influence of a *para*-aza group (dotted line) relative to a *para*-nitro group (solid line) on the potential energy profile for an aromatic nucleophilic substitution as suggested by the present study. (The ground-state levels cannot be fixed in the general case).

150 ml of diethyl ether was added. Insoluble material (sodium chloride) was filtered off and the filtrate was evaporated at room temperature under a dry nitrogen current. The red-brown solid residue, thus obtained, was repeatedly extracted with *n*-pentane. The combined extracts were again evaporated at room temperature under a nitrogen current to yield a yellow solid, mp 53.0–53.5°. On repeated recrystallizations from methanol–water, a pale yellow compound, mp 54.5–55.0°, was obtained in 38% yield. This compound decomposes on standing and is best stored in the cold and away from light.

Anal. Calcd for $C_6H_5N_3O_5$: C, 36.18; H, 2.53; N, 21.10. Found: C, 36.35; H, 2.65; N, 20.53.

Under several conditions, whether as the neat substance or in solution, this compound was found to turn into a high-melting solid on heating, which was identified as N-methyl-3,5-dinitro-4-pyridone, mp 216–219°, lit.[16] 218.5°. Use of a low-boiling extraction solvent (*n*-pentane), a poor solvent for the pyridone, is held responsible for the success of our preparation as compared with the attempts described by the latter authors.

We must note that while the uv spectrum of 3,5-dinitro-4-pyridone shows a maximum at 345 mμ (ϵ 3700) which is shifted to 365 mμ (ϵ 6100) in the presence of CH_3O^-, the uncontaminated 3,5-dinitro-4-methoxypyridine shows no absorption maxima above 230 mμ and in the visible, except for an inflection at about 290 mμ.

Sodium 4-Aza-1,1-dimethoxy-2,6-dinitrocyclohexadienate (Adduct III). 3,5-Dinitro-4-methoxypyridine (nearly 50 mg) was placed in a 5-cm long glass vessel and dissolved in the least amount of methanol at room temperature. A 1 M solution of sodium methoxide was added with a microsyringe in slightly less than the stoichiometric amount. The pale yellow solution turned immediately deep yellow. From the vessel the solvent was removed as fast as possible under vacuum (oil pump). The residue was collected as an orange solid, washed with anhydrous benzene, and finally made solvent-free at 0.1 mm.

Anal. Calcd for $C_6H_5N_3O_5 \cdot CH_3ONa$: C, 33.21; H, 3.19; N, 16.60; Na, 9.09. Found: C, 33.09; H, 3.36; N, 16.47; Na, 9.26.

The solid thus obtained stays unchanged at room temperature in an open vessel and can be safely stored without any special precautions. The physical data for this compound are reported and discussed in the general section.

Physical Measurements. The nmr spectra were obtained on a Varian A-60 spectrometer at 33° (probe temperature), usually at a sweep width equal to 1000; chemical shifts are expressed in parts per million downfield from tetramethylsilane (TMS) as internal standard and are approximate to ±0.02 ppm. The spectra were recorded in the concentration range of 0.5–1.0 M in methanol and in dimethyl sulfoxide solution. Under these conditions the spectrum of the reaction mixture containing the σ complex remained unchanged for hours. The results are reported in the Discussion section.

The visible spectra were obtained on a Beckman DU spectrophotometer; the experiments were performed by using 10.0-mm cells, using methanol as a blank. During the equilibrium and kinetic experiments, the cell housing was kept at constant temperature (±0.1°). The pseudo-first-order rates were determined by the optical density change as a function of time at the appropriate wavelength.

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