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A KINETIC STUDY OF THE *ortho*-MERCURATION OF 2-METHYLAZOBENZENE

PAUL V. ROLING * and RUTH A. PICKERING
Department of Chemistry, Central Michigan University, Mt. Pleasant, MI, 48859 (U.S.A.)

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Summary

The kinetics of the mercuration of 2-methylazobenzene in methanol were studied. The thermodynamic data found were ΔE_{act} = 22.7 kcal mol^{-1}, ΔH^* = 22.0 kcal mol^{-1}, and ΔS^* = —12.3 eu. In comparison with a value of ΔS^* $\approx$ —20 eu for the mercuration of benzene, this lowered entropy is taken as evidence for complex formation between mercuric acetate and 2-methylazobenzene before and during the rate determining step of electrophilic substitution.

Introduction

In a previous paper we looked at the mercuration reaction of azobenzene and *ortho*-substituted azobenzenes [1]. It was found that the major, if not only, result was *ortho*-mercuration. The same result has been found with other metalation reactions of azobenzene [2]. This regiospecificity suggests that the metal is first coordinated by an azo nitrogen and then subsequent electrophilic substitution occurs from this coordination complex (Scheme 1). Assuming that complex formation is fast and reversible and that the concentration of the complex is small, the steady state approximation can be used, producing second order kinetics for the reaction, with the rate determining step being mercury substitution.

An alternate route could be a simple electrophilic substitution with no complex involved (Scheme 2), producing second order kinetics, which is the proposed reaction for the mercuration of benzene [3].

The difference between the two mechanisms is complex formation, which should be reflected in a smaller entropy of activation for the reaction in Scheme 1 versus Scheme 2. In this paper we report the kinetic and thermodynamic data for the mercuration of 2-methylazobenzene. 2-Methylazobenzene was chosen for this

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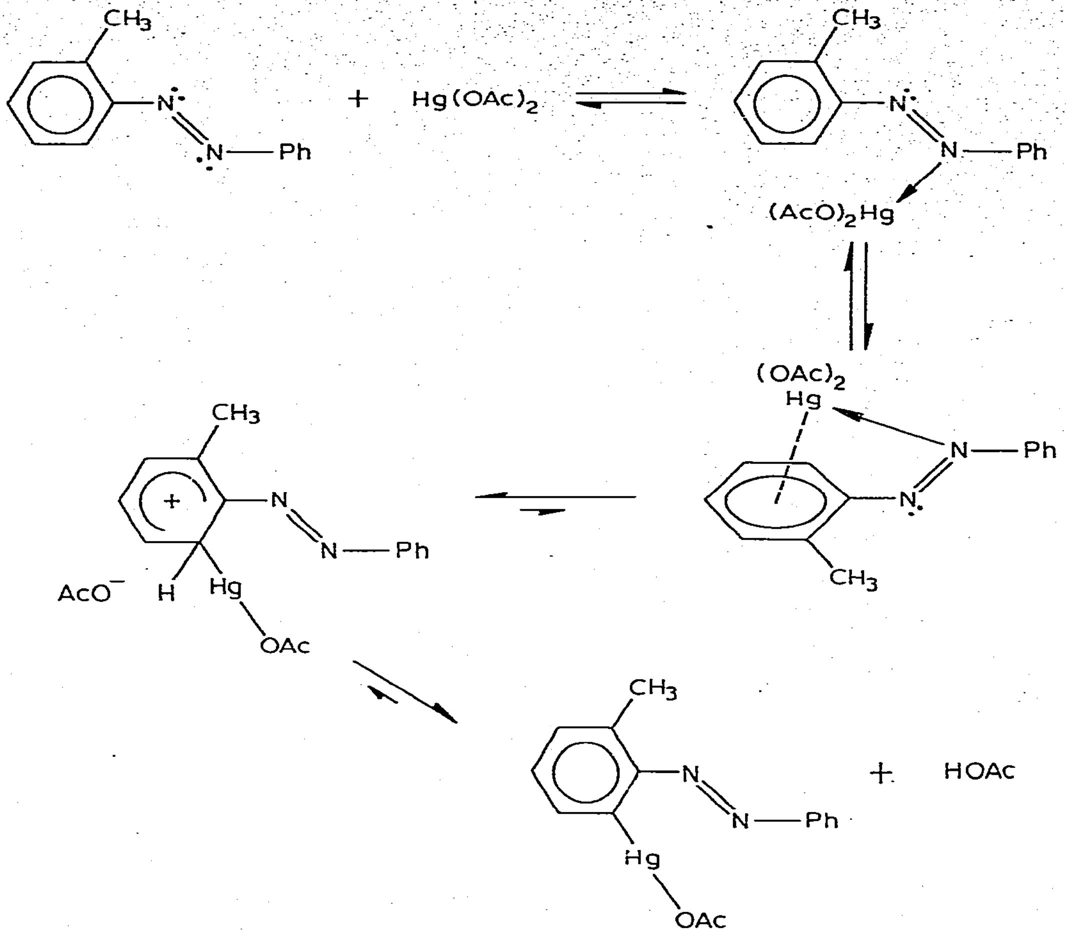
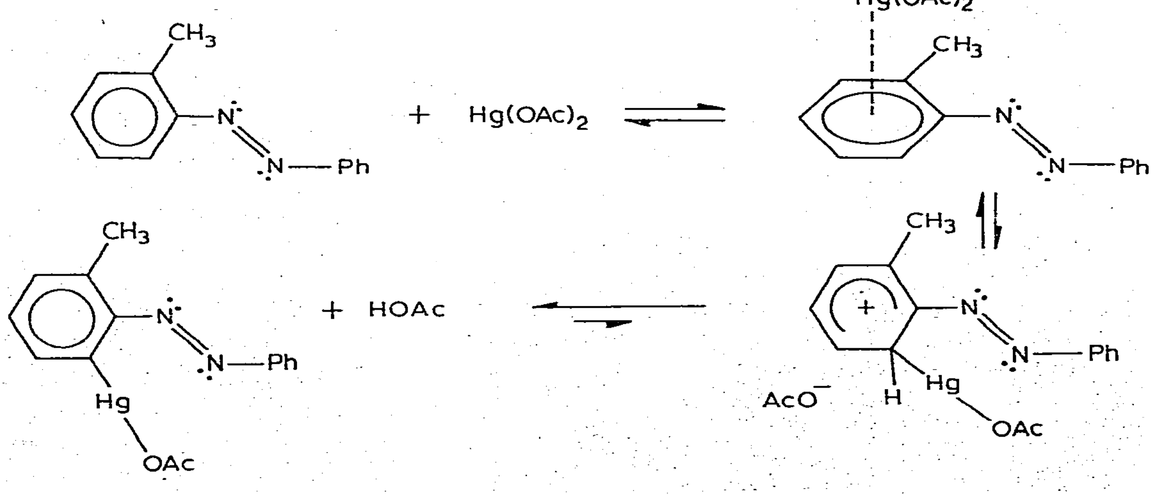
* To whom correspondence should be addressed. Present address: Department of Chemistry, Texas A & M University, College Station, Texas 77843.

SCHEME 1



SCHEME 2



study since it gives, on mercuration, only one product, and that in good yield [1]. All other reactions that we previously studied gave multiple products and/or low yields.

Results and discussion

The rate of mercuration of 2-methylazobenzene with mercuric acetate in methanol was studied at 64, 55, and 45°C. The ratio of mercuric acetate to 2-methylazobenzene was varied from 10 : 1 to 1 : 10. Concentrations of reactants were varied within the range 0.1 *M* to 0.5 *M*. The rates of the reaction were followed by the decrease in mercuric acetate concentrations, determined titrimetrically with standard potassium thiocyanate solution, or in the cases of excess mercuric acetate by separation of the 2-methylazobenzene and spectrophotometric determination of the 2-methylazobenzene.

The rate constants are listed in Table 1. The rate constants were calculated from data measured after 1 h of reaction to 50% reaction. During the first hour, thermal equilibrium was being established, which usually took about 30 min. After 50% reaction, the data began to be inconsistent (a declining rate) due possibly to side reactions. Likewise due to possible side reactions, the rate data from the excess mercuric acetate reactions was not used in thermodynamic data.

The rate data show that the reaction is second order overall, being first order each in 2-methylazobenzene and mercuric actate. This is consistent with the data of Brown et al. [4,5] for the mercuration of aromatic compounds.

Thermodynamic data are listed in Table 2. The ΔE_{act} and ΔH^* for this work are the same as that of Brown and Goldman [5]. However, ΔS^* is considerably lower for the mercuration of 2-methylazobenzene than for the mercuration of benzene or fluorobenzene. Reactions in different solvents with fairly different

TABLE 1

RATE DATA FOR MERCURATION OF 2-METHYLAZOBENZENE IN METHANOL

Run	Initial $(Hg(OAc)_2$ conc'n.	Initial ratio $(Hg(OAc)_2/$ 2-MAB	Temp. (°C)	$k_2{}^a \times 10^5$ (l mol^{-1} sec^{-1})	$k_1{}^b \times 10^5$ (sec^{-1})
1	0.443	9.84	64.0	9.66	4.17
2	0.440	2.02	64.0	9.22	3.54
3	0.448	0.963	64.0	7.42	
4	0.223	1.009	64.0	7.94	
5	0.210	1.014	64.0	7.85	
6	0.117	0.96	64.0	7.65	
7	0.216	0.505	64.0	7.12	2.71
8	0.097	0.100	64.0	7.25	6.78
9	0.410	1.007	54.8	2.43	
10	0.334	1.006	54.8	2.51	
11	0.487	1.008	45.0	1.03	
12	0.375	0.504	45.0	1.39	

[a] The first 1 h was not used in the above calculations since the reaction did not reach thermal equilibrium for about 30 min. Data of over 50% reaction were also not used. Runs 1 and 2 were not used in calculating the thermodynamic data listed in Table 2. [b] These data are the pseudo first order constants.

TABLE 2

THERMODYNAMIC DATA FOR MERCURATION REACTIONS USING MERCURIC ACETATE

Compound mercurated	Solvent	Dielectric constant	ΔE_{act} (kcal mol^{-1})	log A	ΔH^* (kcal mol^{-1})	ΔS^* (cal deg^{-1})
2-Methylazobenzene	Methanol	32.6	22.7	10.59	22.0	−12.3
Benzene [a]	Glacial acetic acid	6.1	22.2	8.91	21.6	−19.6
Fluorobenzene [a]	Glacial acetic acid	6.1	21.3	8.06	20.6	−24.0

[a] Ref. 5.

dielectric constants are being compared and the use of methanol could have some effect in lowering our ΔS^*. However, at this time no definitive work has shown that such a large change in ΔS^* will occur on changing solvents. The lower ΔS^* in our reaction we then take as additional evidence for complex formation as related in Scheme 1.

Experimental

General

The mercuric acetate used was Fisher Certified ACS grade. Fisher Reagent Grade Methanol was used without further purification. The 2-methylazobenzene was made by coupling nitrosobenzene and *o*-toluidine. The compound was purified by column chromatography followed by vacuum distillation, b.p. 111—113°C/ 0.65 mmHg (lit. [7] b.p. 180—181°C/20 mmHg). The NMR spectrum showed only one methyl peak present. Ligroin used was of boiling range 63—75°C. Alumina of activity about 3 was made by shaking 1 kg of activated Fisher Alcoa alumina F-20 with 75 ml of water.

Kinetics (a typical run is given)

In a 100-ml three-necked flask were placed 1.80 g (5.65 mmol) of mercuric acetate, 2.20 g (11.2 mmol) of 2-methylazobenzene and 25 ml of methanol. The mixture was stirred and brought to the appropriate temperature in a constant temperature bath. Aliquots (1.00 ml) were removed by a syringe through a septum as soon as complete solution was achieved (usually within 5 min) and thereafter at 1.0 h intervals. The aliquot was injected into 100 ml of water containing 2 ml of nitric acid in a 125-ml separatory funnel. This solution was quickly and carefully extracted with 15-ml portions of chloroform until the chloroform layer (and the aqueous) was colorless (four extractions). The aqueous layer was then transferred to a flask, 2-drops of a saturated ferric alum solution added, and the solution titrated with a standardized KSCN solution (0.0100 *N*). The KSCN was standardized against silver nitrate. (A weighed amount of mercuric acetate in the above procedure gave a maximum of 1.0% error.)

Typical data for the mercuration of 2-methylazobenzene is presented in Table 3.

The above procedure is of no use when an excess of mercuric acetate is used in the reaction. In these cases, the following modification was employed. The 1.00 ml aliquot was treated as before but the chloroform extracts were collected

TABLE 3

TYPICAL DATA FOR THE RATE OF MERCURATION OF 2-METHYLAZOBENZENE AT 64.0°C

Time (min)	KSCN, 0.0104 M (ml)	Molar concentration[a] of		$k_2{}^b \times 10^5$ ($l\ mol^{-1}\ sec^{-1}$)
		Mercuric acetate	2-Methylazobenzene	
0	41.50	0.216	0.428	
60	37.95	0.197	0.410	
120	34.20	0.178	0.390	7.24
180	31.00	0.161	0.374	7.19
240	28.20	0.147	0.359	7.20
300	25.95	0.135	0.347	7.03
360	23.80	0.124	0.336	7.03
420	21.90	0.114	0.326	7.02
1400	7.40	0.039	0.251	6.70[b]

[a] The concentration of mercuric acetate is determined by the ml of standard KSCN used. The concentration of 2-methylazobenzene is then calculated from the mercuric acetate concentration. [b] The first 60 min of reaction was not used in the calculation of the kinetic data since the reaction did not reach thermal equilibrium for about 30 min. Data of over 50% reaction were also not used. The average value of k_2 is $7.12 \pm 0.10 \times 10^{-5}$ l mol^{-1} sec^{-1}.

and worked-up as follows. The chloroform was evaporated and the residue dissolved in 50 ml of ligroin. This solution was placed on a column of 100 g of alumina of activity about 3. Elution with 3 : 2 ligroin/benzene removed the 2-methylazobenzene, leaving behind the mercurial. The solvent was evaporated and the resulting oil dissolved in 5.00 ml of 95% ethanol. The concentration of 2-methylazobenzene was then determined by its visible absorption at 450 mμ against standards.

2-Acetoxymercuri-6-methylazobenzene

This compound was isolated from the chloroform extracts by evaporation of the chloroform. The solid was extracted once with ligroin to remove any 2-methy azobenzene and then crystallized from benzene to give orange crystals, m.p. 172—174°C. (Found: C, 39.46; H, 2.99; N, 6.04. $C_{15}H_{14}N_2O_2Hg$ calcd.: C, 39.62; H, 3.10; N, 6.16%.)

Acknowledgement

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