

solution, but in this case with only 7% of the stilbene remaining in solution. We believe that at this point the zeolite is saturated with the trans isomer, which can be recovered through extraction in a microsoxlet apparatus. Throughout the experiment essentially all the DMBP is present in solution, and this amount remains constant.

The applications of Silicalite described above bear of course some relation to recent applications of this zeolite for chromatographic purposes for which there are abundant examples.¹⁵⁻¹⁷

The ideas that are illustrated here with photochemical examples can have more general applications in the organic laboratory. In our own work we frequently require very pure samples of *cis*-stilbene and of *m*-terphenyl. The former usually contains some *trans*-stilbene, while *p*-terphenyl is a common impurity in *m*-terphenyl. In both cases the materials can be readily purified by stirring the solution (*m*-terphenyl) or neat material (*cis*-stilbene) with Silicalite.

Registry No. DMBP, 2571-39-3; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; silicalite, 7631-86-9.

(15) Chriswell, C. D.; Chen, Y. Y.; McGowan, C. W.; Markuszewski, R. *J. Chromatogr.* 1987, 405, 213.

(16) Hoering, T. C.; Freeman, D. H. *J. Chromatogr.* 1984, 316, 333.

(17) Campbell, D. J.; Lowe, B. M.; Rowley, A. G.; Williams, R. *Anal. Chim. Acta* 1985, 172, 347.

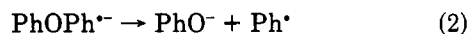
A Kinetic Study of the Reductive Cleavage of Diphenyl Ether by Sodium in Liquid Ammonia

Robert R. Dewald,* Nora J. Conlon, and Woo M. Song

Department of Chemistry, Tufts University, Medford, Massachusetts 02155

Received June 27, 1988

The chemical cleavage of the carbon-oxygen bond in ethers has received considerable attention in the recent literature.¹⁻⁴ In particular, the reductive cleavage of diphenyl ether has been studied under a variety of conditions. Both homogeneous and heterogeneous reductive media result in essentially quantitative cleavage of the starting material to yield phenol and benzene.^{1,2} Thornton, Woolsey, and Bartak¹ have summarized the two most often suggested pathways to achieve cleavage. Both mechanisms involve formation of the radical anion as the first step. The first scheme is consistent with a first-order decomposition of the radical anion to the phenoxide ion and the phenyl radical as shown by eq 1 and 2. This scheme would be consistent with a second-order rate expression, first order with respect to each reactant. A second electron is used in the protonation process. In contrast, the second scheme



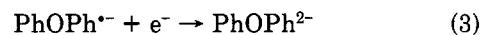
proposes formation of a dianion, either from consecutive electron addition (eq 1 and 3) or by disproportionation of

Table I. Kinetic Data for the Reaction of Diphenyl Ether with Sodium in Liquid Ammonia at -34 °C¹⁰

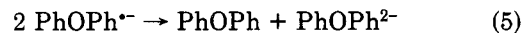
[Na], 10 ⁻⁴ M	[PhOPh], 10 ⁻³ M	k, 10 ² M ⁻¹ s ⁻¹
4.1	6.6	5.0
4.1	0.95	4.4
4.2	2.1	4.3
5.2	1.9	3.5
8.4	1.6	2.4
10.3	1.2	1.9
3.8	2.1	4.3 ^a
5.4	3.6	4.1 ^a
3.1	1.5	7.3 ^a
2.9	1.3	5.8 ^b
9.5	35.0	3.3 ^c

^a NaCl added (9.9 × 10⁻⁴ to 4.7 × 10⁻² M). ^b Cesium used as the metal. ^c 18-Crown-6 added.

the radical anion (eq 1 and 5). It is the dianion that subsequently cleaves to form the phenoxide ion and the phenyl ion (eq 4) that is then protonated. The rate expression for the second scheme should be consistent with a second-order dependence on the electron concentration with eq 3 representing the rate-determining step:



or, alternatively, with eq 5 representing the rate-determining step:



If eq 1 is rate-determining in the second scheme, the rate expression would also be first-order with respect to the electron concentration.

In a recent publication, Thornton, Bartak, and Woolsey¹ reported an electrochemical study of the reduction of diphenyl ether in *N,N*-dimethylformamide (DMF). The cyclic voltammetry experiment at -17 °C exhibited only one reduction peak at potentials up to -3.0 V vs SCE, which was just before breakdown of either the solvent or the supporting electrolyte. On the reverse scan, no reoxidation peak was evident. These results are consistent with a one-electron reduction to form the radical anion followed by a very fast chemical cleavage reaction (eq 1-2). These findings support a previous study by Woolsey and co-workers,² who observed that Na-HMPA reductively cleaved diphenyl ether to form phenoxide and benzene. In both studies, the investigators indirectly detected the phenyl radical.^{1,2}

We report a kinetic study of the reductive cleavage of diphenyl ether by Na in liquid ammonia at -34 °C. This study was undertaken to obtain the rate expression for the homogeneous reduction reaction.

The reaction was studied by the stopped-flow method since, under the conditions of this study, the reduction is too fast to follow by conventional methods. The experimental procedure has been described in detail elsewhere.^{5,6} The disappearance of the ammoniated electron was followed optically by determining the absorption at 1000 nm as a function of time. For experiments run under pseudo-order conditions, plots of the natural log of the electron concentration versus time were found to be linear, indi-

(1) Thornton, T. A.; Woolsey, N. F.; Bartak, D. E. *J. Am. Chem. Soc.* 1986, 108, 6497-6052.

(2) Patel, K. M.; Baltisberger, R. J.; Stenberg, V. I.; Woolsey, N. F. *J. Org. Chem.* 1982, 47, 4250-4254.

(3) Bard, R. R.; Bunnett, J. F.; Creary, X.; Tremelling, M. J. *J. Am. Chem. Soc.* 1980, 102, 2852-2854.

(4) Rossi, R. A.; Bunnett, J. F. *J. Am. Chem. Soc.* 1974, 96, 112-117.

(5) Dewald, R. R.; Brooks, J. M. *Rev. Sci. Instrum.* 1970, 41, 1612-1613.

(6) Brooks, J. M. Ph.D. Dissertation, Tufts University, Medford, MA, 1971.

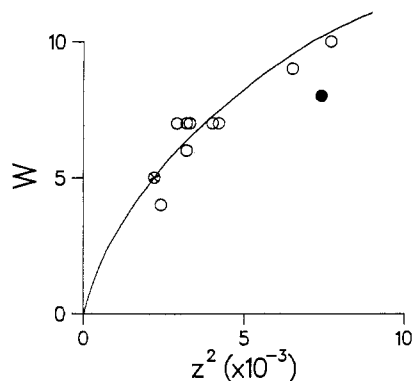


Figure 1. Plot of W versus z^2 for diphenyl ether. Values of z^2 based on initial metal concentration only.¹¹ Closed circle represents experiment with added 18-crown-6. Crossed circle represents experiment with cesium as the metal.

cating a first-order dependence on the electron concentration. In experiments which were not pseudo-order in electron concentration, linear second-order plots indicated a first-order dependence on the diphenyl ether concentration. Combining this information, the reaction was found to follow the rate expression shown as eq 6. The

$$-\frac{1}{2}d[e_{am}^-]/dt = k[e_{am}^-][PhOPh] \quad (6)$$

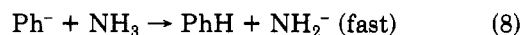
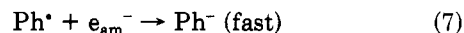
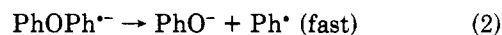
observed second-order rate constants are listed in Table I. Thornton, Woolsey, and Bartak¹ have reported a value of $3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ for the second-order rate constant for the homogeneous electron transfer between the radical anion of acenaphthene and diphenyl ether. This value is of the same order of magnitude as the second-order rate constants we determined for the sodium in liquid ammonia reduction of diphenyl ether. The first-order dependence of the rate on the electron concentration is consistent with a mechanism in which cleavage occurs after formation of the radical anion, that is, after the addition of one electron. A second-order dependence on the e_{am}^- would be indicative of dianion formation prior to cleavage.

As can be seen in Table I, the second-order rate constants vary slightly from one experiment to another. The rate constant did not appear to change markedly when cesium was used as the metal instead of sodium (see Table I). Similarly, when a weighed quantity of NaCl was added to the reaction solution to increase the sodium cation concentration, no significant change in the rate was observed. Upon addition of 18-crown-6, a sodium cation complexing agent, again, no significant change was observed in the rate. These observations are strong indications that the metal cation plays only a spectator role in the reaction mechanism.

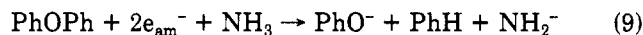
The slight variation seen in the second-order rate constants might well be due to the primary kinetic salt effect as it pertains to the reaction of an ion with a dipolar molecule. To test this supposition, we subjected our kinetic data to the Amis-Jaffe treatment⁷ for the reaction of a negative ion with a dipolar molecule. Amis and Jaffe have developed a dimensionless relationship between W , a function of the natural log of the rate constant, and z , a function of the ionic strength. The reader is referred to the original article⁷ by Amis and Jaffe for further information on this treatment. For our system, the values used to approximate the radius of closest approach, r_0 , and the enhanced dipole moment of diphenylether, μ_0^* , were $4 \times 10^{-8} \text{ cm}$ and 1.10 D respectively. A plot of W vs z^2 provided a smooth curve relationship of appropriate curvature

(Figure 1). This plot is consistent with those shown for the reaction between thiosulfate and ethyl bromomalonate⁸ and for the base hydrolysis of methyl propionate.⁹ It should be noted that z^2 values were calculated by using the initial metal concentration only. When the sodium chloride concentrations were included, the points did not fall on the smooth curve. Reasons for the deviation may be the breakdown of the Amis-Jaffe treatment at high ionic strengths^{8,9} or that the system may exhibit a kinetic salt effect specific to a particular anion,¹² in this case, the electron. From the fit of the data to the Amis-Jaffe treatment, we conclude that the slight variation of the rate constants is in fact due to ionic strength and is typical of a reaction between an anion and a dipolar molecule.

In summary, our kinetic study of the Na-liquid ammonia reduction of diphenyl ether shows a first-order dependence of the rate on both the ammoniated electron and diphenyl ether concentrations, making the reaction second order overall. A first-order dependence on the e_{am}^- is in agreement with the findings of Woolsey and co-workers² and of Thornton, Woolsey, and Bartak.¹ The first mechanistic scheme, which shows cleavage after formation of the radical anion, is consistent with the kinetic data. The complete mechanism is summarized below, including the role of liquid ammonia as the proton source.



The overall reaction is shown below:



We have also found a correlation between the rate and the initial sodium concentration, consistent with the expected primary kinetic salt effect in the reaction of an anion with a dipolar molecule.

Experimental Section

Kinetic experiments were performed using an all-glass, low-temperature, high-vacuum stopped-flow apparatus.^{5,6} Substrate concentrations were determined from weighed quantities of vacuum-distilled diphenyl ether contained in fragile glass ampules, sealed under vacuum, broken into known volumes of liquid ammonia. Metal solution concentrations were determined from initial electrical conductivities compared with published conductivity data.¹³

Acknowledgment. Financial support from the National Science Foundation (Grant CHE-8419961) is gratefully acknowledged.

Registry No. Ph₂O, 101-84-8; Na, 7440-23-5; Cs, 7440-46-2.

(8) Broach, W. J.; Amis, E. S. *J. Chem. Soc.* 1954, 22, 39-42.

(9) Quinlan, J. E.; Amis, E. S. *J. Am. Chem. Soc.* 1955, 77, 4187-4191.

(10) In experiments for which standard deviations of the slope of the least-squares fit of the data were calculated, the values ranged from 0.45% to 1.7%. We are confident that the reported rate constant values are valid to within $\pm 2\%$.

(11) Amis-Jaffe treatment yields a smooth curve relationship only over a limited range of ionic strengths. See ref 8 and 9.

(12) Amis, E. S.; Jaffe, G.; Overman, R. T. *J. Am. Chem. Soc.* 1944, 66, 1823-1826.

(13) Dewald, R. R.; Roberts, J. H. *J. Phys. Chem.* 1968, 72, 4224-4229.

(7) Amis, E. S.; Jaffe, G. *J. Chem. Phys.* 1942, 10, 598-604.