The anomalous accelerating effect of electron-attracting substituents on hydrolysis rate is even more striking in the case of *N*-methylformanilides than in the case of formanilides: *N*-methyl-*m*-nitroformanilide is about ten times as reactive, and *N*-methyl-*p*-nitroformanilide is about a thousand times as reactive, as *N*-methylformanilide. The explanation of the enhanced reactivity of nitro-substituted *N*-methylformanilides is probably the same as for other anilides: strongly electron-attracting aryl substituents cause a change in mechanism from that of Scheme I to that of eq 6. This view is supported by the fact that the effect of the *p*-nitro group on the entropy of activation for hydrolysis of *N*-methyl-*p*-nitroformanilide is similar to its effect on the entropy of activation for hydrolysis of *p*-nitroformanilide: the entropy of activation for *N*-methyl-*p*-nitroformanilide hydrolysis in 0.2 *N* NaOH (−18 eu) is more than 20 eu less negative than that for hydrolysis of a more typical anilide, *N*-methyl-*p*-chloroformanilide (−41 eu).

Registry No.—*m*-Nitroformanilide, 102-38-5; formanilide, 103-07-8; *p*-dimethylaminoformanilide, 18606-63-8; *p*-formylphenoxide ion, 18938-17-5; *p*-nitroacetanilide, 104-04-1.

Acknowledgment.—The authors acknowledge the capable assistance of M. Andrews, W. Duke, A. Imrie, R. Mann, B. Merrick, E. Serros, J. White, and J. Wolf, who measured some of the reaction rate constants reported in Tables II and III.

Reactions of Nitrosobenzene and Azoxybenzene with Benzene, Benzene-d_6, and Cyclohexane at 600°

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Nitrosobenzene reacts with benzene at 200–400° to give mostly azoxybenzene and nitrobenzene. At 500–600° the major products are diphenylamine, biphenyl, phenol, and phenylcarbazoles. Minor products include nitrobenzene, triphenylamine, aminobiphenyl, carbazole, hydroxybiphenyl, diphenyl ether, and aniline. Similar products are formed from azoxybenzene and benzene at 600° with a few exceptions; aniline is a major product and nitrobenzene, triphenylamine, and phenylcarbazoles are not produced. Studies with benzene-d_6 and cyclohexane at 600° showed that in the presence of benzene, nitrosobenzene dissociates to phenyl radical and NO. Disproportionation of nitrosobenzene to azoxybenzene and nitrobenzene occurs in the presence of cyclohexane at 600° but is minor in the presence of benzene.

Although nitrosobenzene and azoxybenzene have been the subject of many investigations, their behavior at elevated temperatures has been relatively unexplored. Bamberger[1] found that nitrosobenzene decomposed at 100° to give mainly azoxybenzene, together with small quantities of nitrobenzene, aniline, *o*-hydroxyazobenzene, and *o*- and *p*-hydroxyazoxybenzene. He proposed that the nitrosobenzene was converted to a mixture of phenylhydroxylamine and nitrobenzene, and the former reacted with nitrosobenzene to give azoxybenzene. Knipscheer[2] pyrolyzed azoxybenzene at 240–250° in the presence of carbon dioxide and obtained 2- and 4-hydroxyazobenzene and azobenzene as products. Dry distillation of azoxybenzene also gave azobenzene along with aniline and nitrosobenzene.[3]

To characterize further the thermal chemistry of nitrosobenzene, we examined its reactions with benzene, benzene-d_6, and cyclohexane. As nitrosobenzene readily gives azoxybenzene, the reactions of azoxybenzene were also studied.

Experimental Section

Experimental procedures and analyses have been described.[4] In a typical experiment, a solution of 19.8 g (0.1 mol) of azoxybenzene and 39 g (0.5 mol) of benzene was pumped into a Vycor tube filled with Vycor chips at 600° under a helium flow of 20 cc/min, with a contact time of 16.1 sec. The vapors were condensed in a flask at 0°; the condensate was distilled to give 32.4 g of benzene and 14.0 g of residue whose analysis is shown in Table II.

Results and Discussion

Nitrosobenzene and Azoxybenzene with Benzene.—The products from the reaction of nitrosobenzene with benzene at 200–600° are listed in Table I. Nitrosobenzene decomposes to nitrobenzene and azoxybenzene at 200–400°, whereas at 500–600° diphenylamine, biphenyl, and carbazoles are the major products. To

TABLE I

REACTION OF NITROSOBENZENE WITH BENZENE[a]

	Relative concentration[b]				
Products	200°	300°	400°	500°	600°
Nitrobenzene	19.1	19.3	17.5	7.1	5.9
Azoxybenzene	76.1	75.7	62.1		
Azobenzene	3.4	3.9	6.5		
Diphenylamine	Trace	0.6	8.2	33.0	34.3
Aminobiphenyls					0.7
Biphenyl			2.7	37.4	30.2
Phenol	1.2	0.5	1.0	8.4	10.1
Diphenyl ether, hydroxybiphenyls					3.6
Carbazole			1.0	1.4	1.2
Phenylcarbazoles			1.0	11.5	12.0
Triphenylamine				1.0	1.4
Aniline				Trace	0.6

[a] Reaction conditions: contact time, 10–19 sec; mole ratio nitrosobenzene:benzene = 1:5. [b] Determined by gas chromatography.

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[1] E. Bamberger, *Ber.*, **35**, 1606 (1902).

[2] H. M. Knipscheer, *Recl. Trav. Chim. Pays-Bas*, **22**, 1 (1903).

[3] E. Bamberger, *Ber.*, **27**, 1182 (1894).

[4] E. K. Fields and S. Meyerson, *J. Org. Chem.*, **33**, 2315 (1968); **35**, 62 (1970).

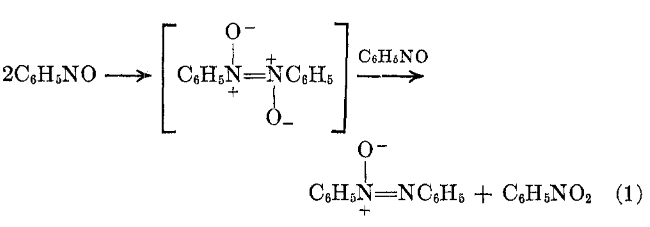
ascertain the fate of azoxybenzene above 500°, we examined the reaction of azoxybenzene with benzene at 600°. A comparison of the products from this reaction with those of the corresponding nitrosobenzene reaction is shown in Table II. Both reactions gave similar products, with some noteworthy exceptions. Aniline was a major product in the azoxybenzene reaction, whereas only trace amounts were obtained from nitrosobenzene. Nitrobenzene and phenylcarbazoles were not observed in the azoxybenzene reaction, and the relative concentration of diphenylamine from this reaction was approximately one-third less than that found in the corresponding nitrosobenzene reaction. The data in Tables I and II suggest that nitrosobenzene is reacting *via* two paths: (1) conversion to azoxybenzene and nitrobenzene followed by the decomposition of azoxybenzene, and (2) decomposition to a phenyl radical and NO. The latter reaction predominates above 400°. We also observed the thermal conversion of nitrosobenzene to azoxybenzene and nitrobenzene at 140–250° in the inlet system of the mass spectrometer.

TABLE II

REACTION OF NITROSOBENZENE AND AZOXYBENZENE WITH BENZENE

Products	Relative concentration[a] Nitrosobenzene[b]	Relative concentration[a] Azoxybenzene[c]
Diphenylamine	34.3	10.0
Aminobiphenyls	0.7	2.8
Biphenyl	30.2	33.8
Phenol	10.1	15.4
Diphenyl ether, hydroxybiphenyls	3.6	2.4
Carbazole	1.2	3.7
Phenylcarbazoles	12.0	
Azobenzene		1.9
Aniline	0.6	30.0
Nitrobenzene	5.9	
Triphenylamine	1.4	

[a] Determined by gas chromatography. [b] Conditions: 600°; contact time, 9.5 sec; mole ratio nitrosobenzene:benzene = 1:5. [c] Conditions: 600°; contact time, 16.1 sec; mole ratio azoxybenzene:benzene = 1:5.

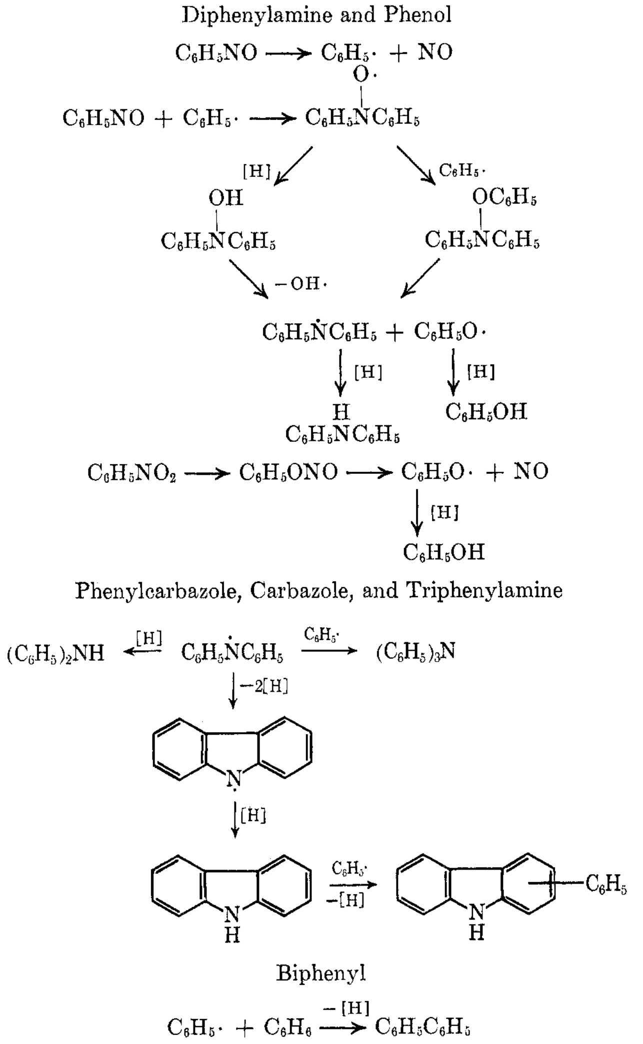


$$2C_6H_5NO \longrightarrow \left[C_6H_5\overset{O^-}{\underset{+}{N}}=\overset{+}{\underset{O^-}{N}}C_6H_5 \right] \xrightarrow{C_6H_5NO} C_6H_5\overset{O^-}{\underset{+}{N}}=NC_6H_5 + C_6H_5NO_2 \quad (1)$$

$$C_6H_5NO \longrightarrow C_6H_5\cdot + NO \quad (2)$$

Nitrosobenzene and Azoxybenzene with Benzene-d_6.—To determine the origin of the phenyl groups in phenol, biphenyl, and the amine products, as well as the partitioning of nitrosobenzene between its dissociation to phenyl radical and NO and its conversion to azoxybenzene, we examined the reaction of nitrosobenzene and azoxybenzene with benzene-d_6 at 600°. The isotopic distribution of the major products is shown in Tables III and IV. Contact times were short enough to avoid appreciable thermal scrambling of protium and deuterium,[5] as evidenced by the deuterium distribution of the recovered benzene. The isotopic distribution of nitrobenzene in Table III indicates that it was derived solely from nitrosobenzene, with the small amount of d_1 component apparently arising by protium–deuterium exchange. The amines, as well as phenol from both reactions, had similar deuterium distributions, chiefly d_0 and d_1 species, with only 5–9% of the diphenylamine and carbazoles arising from reactions involving benzene-d_6 and benzene-

SCHEME I



Diphenylamine and Phenol

Phenylcarbazole, Carbazole, and Triphenylamine

Biphenyl

TABLE III

REACTION OF NITROSOBENZENE WITH BENZENE-d_6[a]

D atoms	Isotopic distribution of products Benzene	Nitrobenzene	Phenol	Biphenyl	Diphenylamine	Carbazole	Phenylcarbazoles
0	0.5	96.1	82.9	2.8	74.7	77.5	77.3
1	0.5	3.9	12.3	1.4	17.1	12.5	15.2
2			1.6		1.5	1.5	2.2
3						1.5	
4	0.5		1.6	4.9	1.5	7.0	3.8
5	6.4		1.6	70.6	5.2		1.5
6	92.1			4.2			
7							
8							
9				2.1			
10				14.0			

[a] At 600°, contact time 10.4 sec; mole ratio nitrosobenzene: benzene = 1:5; isotopic composition of benzene, 0.2% d_4, 5.3% d_5, 94.5% d_6.

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[5] E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **82**, 21 (1966).

TABLE IV

REACTION OF AZOXYBENZENE WITH BENZENE-d_6[a]

	Isotopic distribution of products							
D atoms	Benzene	Phenol	Aniline	Biphenyl	Diphenylamine	Aminobiphenyl	Azobenzene	Carbazole
0	3.1	89.6	86.2	15.2	77.5	71.9	100	74.9
1	0.7	8.5	12.7	4.9	13.3	12.9		13.7
2		0.5	0.8	0.8	1.3	3.5		2.7
3		0.5	0.3	0.2	0.3	0.6		2.5
4	0.5	0.5		4.8	1.1	1.2		6.3
5	7.4	0.4		56.8	5.9	8.8		
6	88.3			4.9	0.6	1.1		
7				0.4				
8				0.2				
9				1.7				
10				10.1				

[a] At 600°, contact time 16.2 sec; mole ratio azoxybenzene:benzene = 1:5; isotopic composition of benzene, 0.5% d_4, 5.8% d_5, 93.7% d_6.

TABLE V

REACTION OF NITROSOBENZENE AND AZOXYBENZENE WITH CYCLOHEXANE

	Relative concentration[d]	
Products[a]	Nitrosobenzene[b]	Azoxybenzene[c]
Diphenylamine	25.5	6.8
Aminobiphenyls	0.5	1.4
Biphenyl	6.9	9.1
Phenol	13.1	31.5
Diphenyl ether, hydroxybiphenyls	2.9	6.5
Nitrobenzene	5.0	1.7
Aniline	39.0	36.7
Carbazole	2.3	2.8
N-Phenylcarbazole	0.7	0.5
Azobenzene	3.3	3.0
Triphenylamine	0.8	

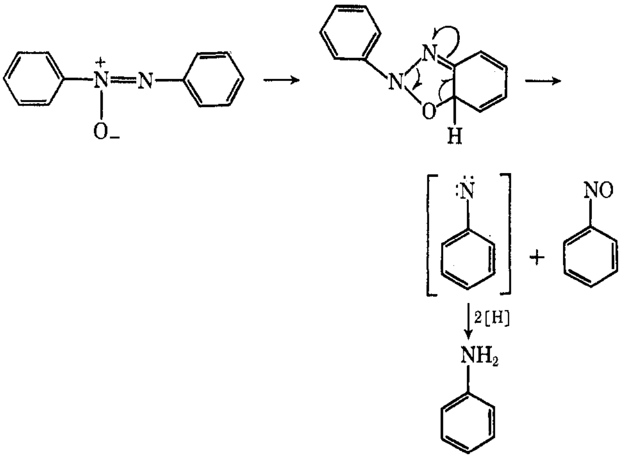
[a] The lower boiling products were benzene, cyclohexadiene, and cyclohexene. [b] At 600°, contact time 16.6 sec; mole ratio nitrosobenzene:cyclohexane = 1:2. [c] At 600°, contact time 20.2 sec; mole ratio azoxybenzene:cyclohexane = 1:4. [d] Determined by gas chromatography.

d_6-derived intermediates. Biphenyl from the nitrosobenzene reaction consisted largely of d_5 and d_{10} species with only 4.2% (d_0 + d_1) originating from nitrosobenzene, whereas biphenyl derived solely from azoxybenzene accounted for 20% (d_0 + d_1) of the total biphenyl. The deuterium distribution of aniline indicated that the aromatic ring was derived solely from azoxybenzene and that azoxybenzene was decomposing to an intermediate which had ready access to hydrogen. Reactions based on the data presented here are suggested in Schemes I and II to account for the major products derived from nitrosobenzene and azoxybenzene, respectively.

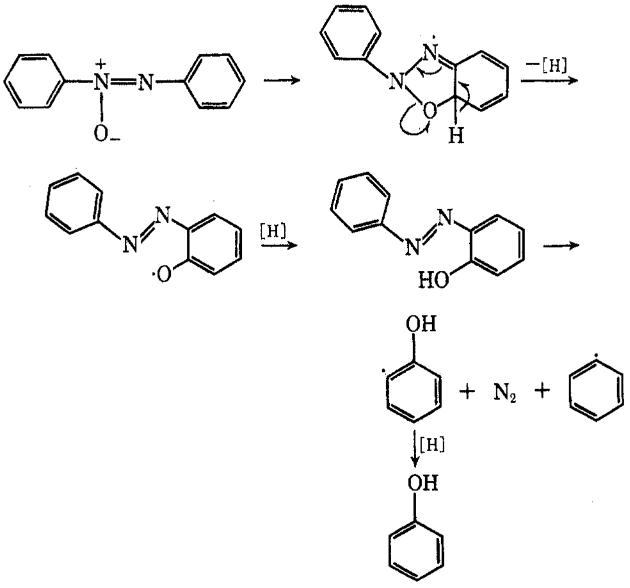
The difference in relative concentrations of aniline and diphenylamine derived from nitrosobenzene and azoxybenzene at 600°, as well as the isotopic distribution of the products from the benzene-d_6 reactions, show that nitrosobenzene dissociates to a phenyl radical and NO. Little nitrosobenzene goes to azoxybenzene above 400°. Nitrosobenzene acts as a trap for phenyl radicals, giving diphenylnitroxide.[6] As a result, less nitrosobenzene is available for conversion to azoxybenzene.

SCHEME II

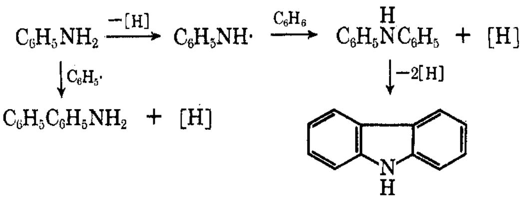
Aniline



Phenol



Diphenylamine, Aminobiphenyl, and Carbazole



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[6] G. R. Chalfont, D. H. Hey, K. S. Y. Liang, and M. J. Perkins, *Chem. Commun.*, 367 (1967); A. Mackor, Th. A. J. W. Wajer, Th. J. deBoer, and J. D. W. van Voorst, *Tetrahedron Lett.*, 2115 (1966).

Nitrosobenzene and Azoxybenzene with Cyclohexane.—To gain additional information concerning the decomposition of nitrosobenzene to phenyl radical and NO and its conversion to azoxybenzene, we carried out the reactions of nitrosobenzene and azoxybenzene with cyclohexane at 600°. As phenyl radical prefers to abstract hydrogen from cyclohexane rather than add to the aromatic ring of benzene at 600°,[7] some of the phenyl radicals generated from nitrosobenzene should be converted to benzene. This should facilitate the conversion of nitrosobenzene to azoxybenzene and its subsequent decomposition to aniline. The data from these reactions are shown in Table V. Aniline indeed was formed as a major product from nitrosobenzene; product distributions from both nitrosobenzene and azoxybenzene with cyclohexane were more nearly the same than those from the corresponding reactions with benzene.

This study shows that the thermal chemistry of nitrosobenzene is quite complex. Dissociation of nitrosobenzene to azoxybenzene and nitrobenzene or to phenyl radicals and NO depends on temperature and the nature of the hydrocarbon used as a reagent.

Registry No.—Nitrosobenzene, 586-96-9; azoxybenzene, 495-48-7; benzene, 71-43-2; benzene-d_6, 1076-43-3; cyclohexane, 110-82-7.

Acknowledgment.—We acknowledge with thanks the assistance of S. Meyerson of Standard Oil of Indiana and D. K. Albert of the American Oil Company for mass spectrometric and gas chromatographic analyses.

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[7] A. I. Feinstein, E. K. Fields, and S. Meyerson, *J. Org. Chem.*, **35**, 303 (1970).

The Basic Hydrolysis of Solubilized Octane-2-diazotate. Dissection of Conservation and Exchange Pathways[1,2]

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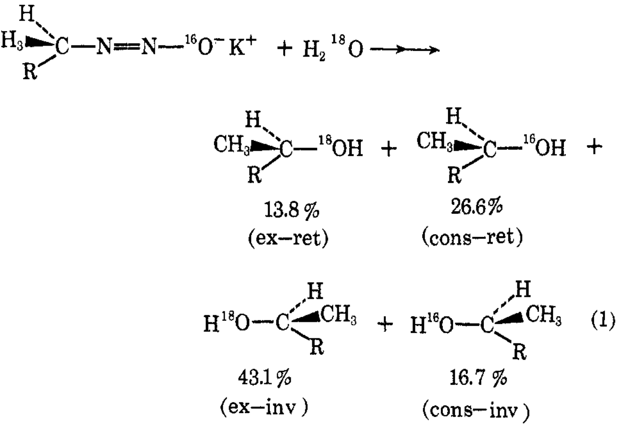
Solubilized optically active octane-2-diazotate (^{16}O) in hexamethylphosphoric triamide–dicyclohexyl-18-crown-6 was hydrolyzed by slow addition to $H_2{}^{18}O$. The resultant 2-octanol was attributed to four product-forming pathways: ^{18}O-incorporation–retention, 18.9%; ^{18}O-incorporation–inversion, 58.5%; ^{16}O-conservation–retention, 16.5%; ^{16}O-conservation–inversion, 6.0%. The results are compared to those obtained upon direct addition of $H_2{}^{18}O$ to solid octane-2-diazotate; mechanisms are discussed.

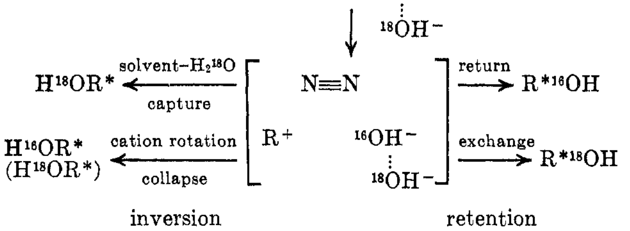
We have analyzed the hydrolysis of optically active potassium octane-2-diazotate (I) with $H_2{}^{18}O$, a reaction which gave the results summarized in eq 1, R = n-C_6H_{13}.[4,5]



Solvent incorporating (exchange) inversion was the predominant pathway (ex–inv product), but substantial conservation of the original diazotate oxygen was also observed. The exchange pathways afforded 2-octanol with 76% overall *inversion*, whereas the conservation pathways afforded 2-octanol with 61% overall *retention*. This pattern, exchange with inversion and conservation with retention, was also observed in the ethanolysis of potassium 1-phenylethanediazotate.[2]

We proposed[4] a mechanism in which $H_2{}^{18}O$ and $^{16}OH^-$ competed for 2-octyl cation in a nonsymmetrically hydrated ion pair (see Scheme I). This mechanism was an adaptation of White's "counterion hypothesis," which has worked well for deaminative processes in nonaqueous solvents.[6]

Scheme I



The previous hydrolyses of I[4,5] involved the addition of water to the solid salt. The ensuing reactions were very rapid on the normal time scale, and the results could have reflected local inhomogeneities in the reac-

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[1] Alkyl Diazotates. IX.[2]

[2] Part VIII: R. A. Moss and M. J. Landon, *J. Amer. Chem. Soc.*, **92**, 5755 (1970).

[3] (a) Fellow of the Alfred P. Sloan Foundation; to whom correspondence should be addressed at Rutgers University. (b) National Science Foundation Undergraduate Research Participant, summer 1970. (c) Colgate-Palmolive Research Center.

[4] R. A. Moss, D. W. Reger, and E. M. Emery, *J. Amer. Chem. Soc.*, **92**, 1366 (1970).

[5] R. A. Moss and S. M. Lane, *ibid.*, **89**, 5655 (1967).

[6] E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, pp 440–483. This excellent review includes a definitive statement of the "counterion hypothesis," as well as elegant illustrations of its applicability.