is not evident with the acetates and perchlorates used in this work. Apparently the "special salt effect" is negligibly small in the solvolysis of acetyl chloride in glacial acetic acid.

The Effect of Solvent.—The work reported here extends the range of solvents in which the solvolysis of acetyl chloride has been measured. The plot of log *k vs. Y*, Fig. 2, shows some major deviations from Winstein's *mY* relation.[13] Thus the acetic acid points do not lie on the acetone–water line, and both lines apparently show a large curvature in the region of high water concentration. These deviations are of the same types commonly shown in the solvolysis of other compounds,[37] but they are unusually large. The deviations at high water concentrations are probably due more to differences between the reactants, acetyl chloride and *t*-butyl chloride, than to differences in the transition states for solvolysis. Thus acetyl chloride probably does not show a large increase in activity coefficient over the range from pure acetic acid to pure water whereas *t*-butyl chloride shows a 4000-fold increase in its Henry's law constant[13] over this range of solvents.

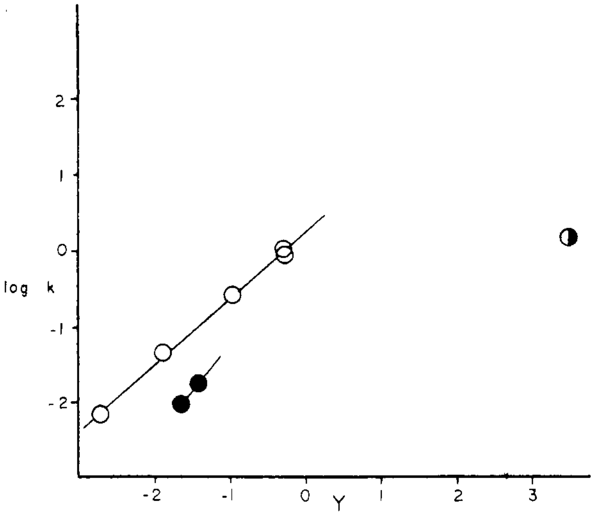

Fig. 2.—Rate constants at 25° for the solvolysis of acetyl chloride *vs.* Wintsein's *Y* values.[7] ●, this work; ◑, pure water, Gold and Hilton[16] corrected to 25°; ○, acetone–water mixtures, data from ref. 18, 19, and 20.

[37] S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957).

Kinetics of the Sodium Alkoxide Reduction of Nitrobenzenes

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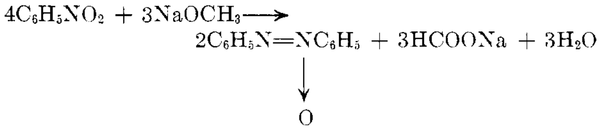
The rates of the reduction of nitrobenzene by sodium methoxide in methanol in a nitrogen atmosphere to form azoxybenzene were followed by the acidimetry of methoxide and by spectrophotometry of the aromatic compounds. The rates were expressed as $v = k[PhNO_2][CH_3ONa]^2$. Methanol was oxidized to formic acid and formaldehyde, formaldehyde then being gradually transformed to methyl formate and other products. Gaseous oxygen, hydrogen peroxide, benzoyl peroxide, and water retarded the reduction, while 9-fluorenone accelerated it. A mechanism (equations 1, 2, 5, and 7) was postulated, which involves simultaneous rate-determining attacks of two molecules of sodium methoxide to nitrobenzene, followed by a rapid condensation of the products, nitrosobenzene and phenylhydroxylamine. The rates of reduction of nitrobenzene by some other sodium alkoxides increased in the order: $CH_3ONa < C_2H_5ONa < n\text{-}C_3H_7ONa$. The electron-releasing group (p-CH_3O) in nitrobenzene retarded the reduction, while the electron-attracting group (m-NO_2) accelerated it.

It is well known that nitrobenzene is reduced to azoxybenzene by sodium alkoxide according to the stoichiometric equation[1]



$$4C_6H_5NO_2 + 3NaOCH_3 \longrightarrow 2C_6H_5\underset{\underset{O}{\downarrow}}{N}{=}NC_6H_5 + 3HCOONa + 3H_2O$$

It is probable that the reaction involves the condensation of phenylhydroxylamine and nitrosobenzene both produced by the reduction of nitrobenzene.[2,3] However, very little is known about the kinetics and mechanism of this reaction.

The present paper summarizes our data on the kinetic investigation on the reduction of nitrobenzene and ring-substituted nitrobenzenes by sodium methoxide, ethoxide, or propoxide. The rates of the consumption of alkoxide were followed by acidimetry and those of aromatic compounds by ultraviolet spectrophotometry. It was found that formaldehyde as well as formic acid was produced during the reaction, formaldehyde being then converted to methyl formate and other products in the presence of sodium methoxide. The concentration of formaldehyde was determined by the sulfite method.

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[1] H. S. Fry and J. L. Cameron, *J. Am. Chem. Soc.*, **49**, 864 (1927).

[2] E. Bamberger and E. Renauld, *Ber.*, **30**, 2278 (1897); E. Bamberger and A. Rising, *Ann.*, **316**, 257 (1901).

[3] Y. Ogata, M. Tsuchida, and Y. Takagi, *J. Am. Chem. Soc.*, **79**, 3397 (1957).

Experimental

Materials.—All materials used were purified by rectification when they were liquid, and by recrystallization when they were solid. Phenylhydroxylamine was prepared by the reduction of nitrobenzene and recrystallized before use from a mixture of benzene and petroleum ether,[4] m.p. 82°.

The Reaction Products Criterion.—The presence of formaldehyde in the reaction mixture was detected by means of Schiff's reagent and also the silver mirror test. Furthermore, it was identified as the 2,4-dinitrophenylhydrazone, m.p. and mixture m.p. 165°.

Nitrobenzene was reduced with alkoxides under the kinetic conditions and gave azoxybenzene, m.p. and mixture m.p. 37°. The reduction of *m*-dinitrobenzene with sodium methoxide at the boiling temperature of methanol gave *m,m'*-dinitroazoxybenzene (38%), m.p. and lit.[5] m.p. 142°. Similar reduction of *p*-nitroanisole gave *p,p'*-dimethoxyazoxybenzene (79.0%), m.p. and lit.[6] m.p. 114–116°.

The Conversion of Formaldehyde.—Methyl formate, the conversion product of formaldehyde, was identified as follows. A solution of paraformaldehyde in methanolic sodium methoxide was warmed at 60°, the distillate, methyl formate and methanol, b.p. 31.5–32.5°, being collected by cooling with Dry Ice–methanol. One milliliter of the distillate was diluted with water to 20 ml., 1 g. of mercuric oxide was added, and the mixture was shaken at 45° and filtered. On boiling the filtrate, a gray precipitate of mercury was observed, which indicated the presence of formic acid. The same behavior was observed with authentic methyl formate. The distillate contained no formaldehyde on the sulfite test. The conversion of formaldehyde to methyl formate, methanol, and sodium formate was estimated to be *ca.* 72% on the basis of the saponification value of the distillate and the acidimetry of the remaining solution.

Quantitative Analyses. (a) Spectrophotometry.—A standard methanolic solution of known amounts of azoxybenzene and nitrobenzene was analyzed by means of ultraviolet spectrophotometry. After confirming that the standard solutions obey Beer's law, the reaction mixture was diluted with methanol to *ca.* 10^{-4} *M*, both components being determined at wave lengths of 260, 280, and 320 mμ.[3]

(b) Acidimetry.—The concentration of remaining sodium alkoxide was measured by acidimetry with hydrochloric acid and Bromothymol Blue. The amount of alkoxide consumed corresponded to the formic acid produced, which was confirmed by a blank test with a reaction mixture. The concentration of formaldehyde was determined by the sulfite method—*i.e.*, after neutralization of the reaction solution with aqueous hydrochloric acid using rosolic acid as an indicator, an aqueous solution of 0.5 *N* sodium sulfite was added, then the amount of alkali produced was titrated with 0.05 *N* aqueous hydrochloric acid.

Typical Procedure for Rate Measurements.—In a three-necked flask equipped with an ice water-cooled reflux condenser bearing a calcium chloride tube, a tube for introducing nitrogen, and a tube for withdrawing samples was placed a methanolic solution of nitrobenzene, the flask being kept at 69.0 ± 0.1°. A methanolic solution of sodium methoxide kept at the same temperature was poured into the solution. In general the reaction started after an induction period of 0–30 min. depending mainly on the concentration of alkoxide. Aliquots were taken at appropriate time intervals, the contents being analyzed as stated above. It was confirmed that the vaporization loss of methanol was less than 1%. The reaction was sensitive to atmospheric oxygen; hence most experiments were carried out in nitrogen atmosphere.

Results

Stoichiometry.—Table I shows concentrations of reactants and products at known time intervals. As apparent in the table, one mole of azoxybenzene is formed by the consumption of two moles of nitrobenzene; the formation of three moles of formic acid and formaldehyde corresponds to the formation of two moles and one mole of azoxybenzene respectively, as expected from the stoichiometry of equations:

$$3CH_3ONa + 4PhNO_2 \longrightarrow 2PhNO{=}NPh + 3HCOONa + 3H_2O$$

$$3CH_3ONa + 2PhNO_2 \longrightarrow PhNO{=}NPh + 3HCHO + 3NaOH$$

i.e. (formed PhNO=NPh in *M*) = $^2/_3$ (formed HCOOH in *M*) + $^1/_3$ (formed HCHO in *M*). Since a part of the produced formaldehyde is converted to other products, the ratio β tends to deviate from unity with time (see Table I).

Reduction Rates.—The reduction rates of nitrobenzene were found to fit the third-order equation:

$$-d[PhNO_2]/dt = k[PhNO_2][CH_3ONa]^2$$

The rate constant, *k*, was calculated graphically as exemplified in Table II. Table III shows *k* values with various initial concentrations of reactants; $[\ ]_0$ enclosing the formula indicates its initial molar concentration. The data do not satisfy the second-order equation.

The Rate of Conversion of Formaldehyde by Sodium Methoxide.—The rate of conversion of formaldehyde to methyl formate (equation 8) in pure methanol under the kinetic conditions estimated by the sulfite method was found to be expressed by the second-order equation:

$$v = k_8[HCHO]\ [CH_3ONa]$$

The average k_8 value thus obtained was 6.97×10^{-4} M^{-1} min.$^{-1}$ at 69.0°, with $[HCHO]_0 = 0.199 - 0.213\ M$ and $[CH_3ONa]_0 = 0.671 - 1.48\ M$. However, it was found that the k_8 value varies with changing amount of water added to the solution, owing to the contribution of Cannizaro reaction. Thus with $[H_2O] = 0.327\ M$, the average k_8 was 5.76×10^{-3} at 69°. The stoichiometric equation requires that 0.346 (= 0.461 × $^3/_4$) *M* of water is formed at 92 min. by the reduction of (1.794 − 1.333 =) 0.461 *M* of nitrobenzene. Therefore, k_8 was assumed to be 5.76×10^{-3} M^{-1} min.$^{-1}$ at 92 min.

The Rate of Formation of Nitrosobenzene.—If formaldehyde is produced in the present reduction from nitrobenzene (equation 1), then the rate constant k_1 may be calculated from the available values of d[HCHO]/d*t* and k_8 (= 5.76 × 10^{-3} M^{-1} min.$^{-1}$ at 92 min.) by means of the equation:

$$d[HCHO]/dt = k_1[PhNO_2][CH_3ONa]^2 - k_8[HCHO][CH_3ONa]$$

The data are shown in Table IV. Therefore, k_1/k = 0.486 or the rate of formation of azoxybenzene is twice as large as the rate of formation of nitrosobenzene. Furthermore, since $[HCHO]_0$ is 0, the k_1 value at $t = 0$ can be calculated to be 2.10×10^{-4} from the extrapolated values of d[HCHO]/d*t*, $[PhNO_2]_0$ and $[CH_3ONa]_0$, using the above equation; hence, the value agreed with that at 92 min. Thus it is apparent that the k_1 value varies very little with time, although the stoichiometric equation may not exactly be satisfied.

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[4] O. Kamm, *Org. Syntheses*, Coll. Vol. I, 445 (1941).

[5] H. Klinger and R. Pitschke, *Ber.*, **18**, 2551 (1885).

[6] D. Vorländer, *ibid.*, **40**, 1422 (1907).

TABLE I

THE MATERIAL BALANCE FOR THE AZOXYBENZENE FORMATION

Reaction time in min.	0	92	156	236	Theoretical
$[PhNO_2]$ in M	1.794	1.333	1.236	1.083	
$[PhNO{=}NPh]$	0.000	0.202	0.281	0.359	
$[CH_3ONa]$ in M	2.759	2.530	2.429	2.342	
$[HCHO]$ in M	0.000	0.127	0.120	0.112	
α[a]	...	2.28	1.99	1.98	2.00
β[b]	...	0.97	0.93	0.88	1.00

[a] Consumed nitrobenzene in M/formed azoxybenzene in M. [b] [2(Consumed CH_3ONa in M) + (formed HCHO in M)]/[3(formed $PhNO{=}NPh$ in M)].

TABLE II

THIRD-ORDER RATE CONSTANTS k AT VARIOUS TIMES

$[CH_3ONa]_0 = 2.49\ M$, $[PhNO_2]_0 = 0.391\ M$, temp.: 69.0 ± 0.1°

Time in min.	90	180	240	300	Av.
$k \times 10^4$ in M^{-2} min.$^{-1}$	4.21	4.51	3.90	3.94	4.14

TABLE III

THIRD-ORDER RATE CONSTANTS k WITH VARIOUS INITIAL CONCENTRATIONS AT 69.0°

$[CH_3ONa]_0$ in M	1.37	1.79	2.49	2.84	3.29	
$[PhNO_2]_0$ in M	1.89	1.89	0.391	0.391	1.95	Av.
$k \times 10^4$ in M^{-2} min.$^{-1}$	4.23	4.17	4.14	4.50	4.26	4.26

TABLE IV

THIRD-ORDER RATE CONSTANTS k_1 FOR THE FORMATION OF NITROSOBENZENE AT 69.0°

$[PhNO_2]_0$	$[CH_3ONa]_0$	$[HCHO]_0$	$k_1 \times 10^4\ M^{-2}$ min.$^{-1}$
1.33 M	2.53 M	0.127 M	2.04
1.23	2.43	0.120	2.16

The Effects of Additives.—Table V shows the effects of several additives on the rate of reduction measured spectrophotometrically. It is of interest to note that oxidizing agents and water retard or inhibit the reduction, and that 9-fluorenone accelerates it.

TABLE V

THE EFFECTS OF ADDITIVES ON THE REDUCTION RATE

Additive	Effect E,[a] Reaction Time in Min.		
Water, 8 vol. %	0.25 (60)	0.69 (120)	0.76 (240)
Water, 16 vol. %	0.00 (60)	0.16 (120)	0.14 (240)
Benzoyl peroxide, $7.38 \times 10^{-3}\ M$	0.75 (150)	0.49 (330)	
Benzoic acid, $1.19 \times 10^{-4}\ M$	1.00 (150)	0.65 (330)	
MnO_2, 43.4 mg./25 ml. soln.	0.94 (120)	0.86 (270)	
30% aq. H_2O_2, 0.4 vol. %	0.74 (240)	0.99 (480)	
30% aq. H_2O_2, 0.8 vol. %	0.66 (240)	0.91 (480)	
9-Fluorenone, $4.93 \times 10^{-3}\ M$		1.10 (85)	1.68 (175)
9-Fluorenone, $8.14 \times 10^{-3}\ M$		1.59 (120)	1.77 (180)

[a] E = ($[PhNO{=}NPh]$ in the presence of additive)/($[PhNO{=}NPh]$ without additive).

The Solvent Effect.—Ethanol–sodium ethoxide or n-propyl alcohol–sodium n-propoxide was used instead of methanol–sodium methoxide. The reactions with these alkoxides occurred even in solutions so dilute that the reaction would not have been appreciable with methoxide—*e.g.*, with 0.713 M of $[C_2H_5ONa]_0$ or 1.06 M of $[n{-}C_3H_7ONa]_0$ for 0.751 M of nitrobenzene, where k values for ethoxide and propoxide were calculated to be 6.7×10^{-3} and $1.3 \times 10^{-2}\ M^{-2}$ min.$^{-1}$, respectively. Hence, the rate of the reaction decreased in the order: n-PrOH>EtOH>MeOH. However, the reductions with ethoxide and propoxide seem to have some side reactions such as the azobenzene formation, since the reaction mixture became dark colored and the stoichiometry between formed azoxybenzene and consumed nitrobenzene deviated 10–15% from the theoretical value. No reaction occurred with isopropyl alcohol because of the low solubility of the alkoxide.

The Effect of Atmospheric Oxygen.—The presence of oxygen gas in the reaction vessel elongated the induction period, while the replacement of the atmosphere with gaseous nitrogen shortened the induction period, when $[CH_3ONa]_0$ was 3.5–2.9 M as shown in Table VI. A long induction period was observed when $[CH_3ONa]_0$ was less than 1.0 M even in nitrogen atmosphere, while no difference between the reaction in air and that in nitrogen was observed, when $[CH_3ONa]_0$ was larger than 3.7 M.

TABLE VI

THE EFFECT OF ATMOSPHERIC OXYGEN AT 69.0°

$[CH_3ONa]_0$ in M	Effect B,[a] Reaction Time in Min.	
2.94	0.38 (150)	0.44 (150)
3.51	0.80 (120)	0.90 (270)
3.74	0.97 (120)	0.89 (270)

[a] B = (Consumed nitrobenzene in M under air)/(Consumed nitrobenzene in M under nitrogen atmosphere).

The Substituent Effect.—Since the spectrophotometric analyses failed with substituted nitrobenzenes, the substituent effect was compared qualitatively. No reaction was observed with p-nitroanisol (0.200 M) for $[CH_3ONa]_0$ = 1.32 or 2.24 M on refluxing for 20 hr., although with more concentrated sodium methoxide ($[CH_3ONa]_0$ = 4.35 M for 0.428 M of p-nitroanisol) gave p,p'-dimethoxyazoxybenzene (79.0%). m-Dinitrobenzene (0.527 M) and sodium methoxide ($[CH_3ONa]_0$ = 0.695 M) readily gave m,m'-dinitroazoxybenzene (34.8%), while no reaction occurred with nitrobenzene under these conditions. p-Chloronitrobenzene and p-nitrotoluene gave p-methoxynitrobenzene and p,p'-dinitrobibenzyl, respectively, as a main product under these conditions.

The Reaction of Phenylhydroxylamine and Nitrobenzene.—In order to prove the validity of reaction 5, a mixture of nitrobenzene (3.4×10^{-4} *M*), phenylhydroxylamine (8.5×10^{-4} *M*), and sodium methoxide (0.379 *M*) was refluxed in a solution of methanol for 2 hr. There was obtained azoxybenzene (0.5×10^{-4} *M*), the decreased concentrations of nitrobenzene and phenylhydroxylamine being 0.2×10^{-4} and 0.9×10^{-4} *M*, respectively (spectrophotometric estimations). The reaction of nitrobenzene with sodium methoxide in the absence of phenylhydroxylamine did not occur under these conditions.

Discussion

The rate of condensation of phenylhydroxylamine with nitrosobenzene to form azoxybenzene is very fast compared with the reduction rate of nitrobenzene[3] and neither nitrosobenzene nor phenylhydroxylamine was detected in the present reaction mixture; hence the reduction step of nitrobenzene with sodium methoxide should be rate-determining. Here, the attacking agent may be CH_3ONa instead of CH_3O^-, because lowering the concentration of methoxide (causing more complete dissociation) or the addition of a small amount of water retards the reaction. The reaction of nitrobenzene with sodium methoxide is second-order in methoxide: $-d[PhNO_2]/dt = k [PhNO_2] [CH_3ONa]^2$. Formaldehyde and formic acid were produced during the reduction.

These facts suggest following steps for the formation of nitrosobenzene and phenylhydroxylamine, respectively.

$$PhNO_2 + 2CH_3ONa \xrightarrow{k_1} PhNO + HCHO + NaOH + CH_3ONa \quad (1)$$

$$PhNO_2 + 2CH_3ONa \xrightarrow{k_2} PhNHOH + HCOONa + CH_3ONa \quad (2)$$

Since the equimolar formation of formaldehyde (or nitrosobenzene) and formic acid (or phenylhydroxylamine) is not conceivable, either reduction, $PhNO \rightarrow PhNHOH$, or oxidation, $PhNHOH \rightarrow PhNO$, occurs. For the reduction of nitrosobenzene, the following equation is possible.

$$PhNO + CH_3OH \xrightarrow{CH_3ONa} PhNHOH + HCHO \quad (3)$$

or

$$PhNO + HCHO + NaOH \longrightarrow PhNHOH + HCOONa \quad (4)$$

and for the oxidation of phenylhydroxylamine

$$PhNHOH + PhNO_2 \longrightarrow 2PhNO + H_2O \quad (5)$$

or

$$PhNHOH + {}^1/_2O_2 \longrightarrow PhNO + H_2O \quad (6)$$

Mechanism (1 + 3) should produce formaldehyde alone in the reduction, and the formation of a large amount of formic acid would be inexplicable. Mechanism (1 + 4) requires that step 4 should be much faster than step 1, since no nitrosobenzene is detectable, hence no formaldehyde would be detected during the reduction. But this requirement was not fulfilled as stated above. Furthermore, it was confirmed in our hands that the reaction of nitrosobenzene with sodium methoxide gave neither phenylhydroxylamine nor azoxybenzene.

Since the reduction proceeds more easily in a nitrogen atmosphere, mechanism 5 is more probable than 6. Therefore, mechanism (1 + 2) followed by step 5 should be the most probable mechanism, with Equation 2 a little faster than Equation 1; thence the excess of phenylhydroxylamine remaining after the very rapid condensation with nitrosobenzene should be oxidized rapidly to nitrosobenzene with nitrobenzene. These condensation and oxidation should be faster than reaction 2, since no phenylhydroxylamine was detected by spectrophotometry.

Hence the over-all mechanism is expressed as

$$PhNO_2 + 2CH_3ONa \xrightarrow{k_1} PhNO + HCHO + NaOH + CH_3ONa \quad (1)$$

$$PhNO_2 + 2CH_3ONa \xrightarrow{k_2} PhNHOH + HCOONa + CH_3ONa \quad (2)$$

$$PhNHOH + PhNO_2 \xrightarrow{k_5} 2PhNO + H_2O \quad (5)$$

$$PhNHOH + PhNO \xrightarrow{k_7} PhNO{=}NPh + H_2O \quad (7)$$

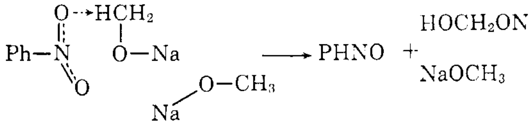
Formaldehyde is converted to methyl formate or other products, *e.g.*, methanol and formic acid in the presence of water, under the kinetic conditions as described in experimental part.

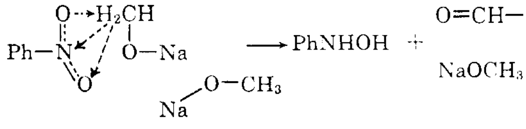
$$2HCHO \xrightarrow{CH_3ONa} HCOOCH_3 \quad (8a)$$

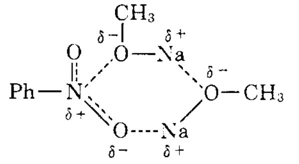
$$\xrightarrow{H_2O} HCOOH + CH_3OH \quad (8b)$$

Reactions similar to 8a have been reported in the aluminum methoxide–catalyzed condensation of formaldehyde[7] or sodium methoxide–catalyzed condensation of benzaldehyde.[8]

The second-order dependence of the rate with alkoxide suggests transition states for equations 1 and 2, respectively:


(1')


(2')


(I)

The energy of the transition state may be decreased by the formation of six-membered ring (I). This second-order dependence with alkoxide has been observed in the Meerwein-Ponndorf reduction with aluminum alkoxide.[9]

The retardation observed by the addition of benzoyl peroxide or hydrogen peroxide may be due to the suppression of hydrogen atom transfer; the acceleration by the addition of 9-fluorenone implies its role as a hydrogen atom carrier. The role of 9-fluorenone as a hydride-ion carrier[10] is less probable because of the observed retardation of the reaction on addition of peroxides. Our observation that the addition of benzoquinone or hydroquinone could not produce the retardation may be due to their easy transformation into black amorphous oxidation products in the present reaction mixture.

The tendency of an electron-withdrawing group in nitrobenzene to accelerate the reaction coincides with the above nucleophilic attack of sodium methoxide molecule on the nitrogen atom of nitrobenzene.

(7) V. Tischenko, *J. Russ. Phys. Chem. Soc.*, **38**, 355 (1906); *Chem. Zentr.*, II, 1310 (1906).

(8) L. Claisen, *Ber.*, **20**, 646 (1887).

(9) W. N. Noulton, R. E. Van Atta, and R. R. Ruch, *J. Org. Chem.*, **26**, 290 (1961).

(10) A. A. Sayigh, *ibid.*, **25**, 1707 (1960).

The Dipole Moment and Structure of Thiolactams

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Measurement of the dipole moments of thiolactams in dioxane at 30° gives the following: thiopyrrolidone I, 5.07 D; thiopiperiodone II, 5.15 D, and thiocaprolactam III, 4.83 D. Comparison of the moments of I, II, and III with the moments of corresponding lactams shows that the thiolactams have dipole moments about 1.0–1.3 D. higher. This is due to the greater inherent polarization of the thiocarbonyl group which is also indicated by the lower infrared stretching frequency and the lower maxima and greater extinction in the ultraviolet. These data indicate that there is more of the ionic form $\overset{+}{C}—\overset{-}{X}$ (X = S or O) present in thiolactams than in lactams.

Sulfur and oxygen are isoelectric, *i.e.*, in their outermost shell they both have two *s* and four *p* electrons. Both sulfur and oxygen would thus be expected to be capable of forming two single or one double bond.

Sanderson[1] has pointed out the major differences that affect the chemistry of the two elements. The kernel of ten electrons in sulfur compared to only two electrons in oxygen makes sulfur more likely to form single bonds than multiple bonds. The greater size of the covalent radii of sulfur compared to oxygen (1.02 Å. compared to 0.73 Å.) causes the electronegativity of sulfur to be less than oxygen (2.5 compared with 3.5[2]). Another difference is the ability, completely absent in oxygen atoms, of sulfur atoms to utilize its outer 3 *d* orbitals.

These differences would be expected to have a pronounced effect on the electronic distribution of thiolactams compared with lactams. This difference is reflected in the dipole moments, infrared and ultraviolet spectra of the thiolactams.

Results and Discussion

Table I gives the dipole moments of thiopyrrolidone I, thiopiperidone II, and thiocaprolactam III in dioxane at 30° along with the previously determined moments of the carbonyl analogs. In all three cases, the moments of the thiolactams are higher than those of the corresponding lactams.

TABLE I

DIPOLE MOMENT OF THIOLACTAMS AND LACTAMS IN DIOXANE AT 30° AND INFRARED THIOCARBONYL AND CARBONYL FREQUENCIES[a]

I.	5.07 D Thiopyrrolidone 1115 cm.$^{-1}$	3.79 D Pyrrolidone[b] 1706 cm.$^{-1}$
II.	5.15 D Thiopiperidone 1112 cm.$^{-1}$	3.83 D Piperidone[c] (benzene 25°) 1672 cm.$^{-1}$
III.	4.83 D Thiocaprolactam 1117 cm.$^{-1}$	3.88 D Caprolactam[c,d] (benzene 25°) 1669 cm.$^{-1}$
Moment of thiolactam minus moment of lactam		1.28 D 1.32 D 0.95 D

[a] See ref. 9. [b] See ref. 10. [c] See ref. 11. [d] See ref. 12.

The lower electronegativity of sulfur compared to oxygen might have been expected to cause a decrease in the moment of the thiolactam com-

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(1) R. T. Sanderson, "Chemical Periodicity," Reinhold, New York, 1960, p. 208.

(2) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, 1960, p. 90.