

Effect of the Solvent on the Kinetics of Diazotization^{1a}

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It is shown in methanol-carbon tetrachloride mixtures at 0° that the reaction rate expression developed for diazotization of aniline in pure methanol by Schmid, *et al.*, is further resolvable. Omitting simplifying assumptions concerning the degree of dissociation of the electrolytes present in the reaction mixture, one can detect protonic catalysis which was not found in the earlier work. A rate equation involving H⁺ catalysis is presented. This equation follows automatically from Schmid's reaction mechanism proposed in methanol, that can be confirmed also in methanol-carbon tetrachloride mixtures up to 60% CCl₄ v/v (*D*₀^o = 15.00). For solvents with lower dielectric constant, the possibility of Ph·NH·NO → Ph·N:N·OH being rate controlling is suggested. Kinetic data have been obtained in pure carbon tetrachloride using an extrapolation method, although the reaction is heterogeneous in this medium. The effect of changing dielectric constant of solvent on the reaction rate is also discussed.

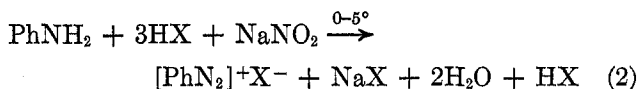
Introduction

The kinetics and mechanism of diazotization in aqueous solution is well described through the works of Ingold, *et al.*, and Schmid, *et al.*² The latter also investigated this reaction in methanol.³ Summarizing the results obtained in water and in methanol, diazotization is the N-nitrosation of primary aromatic amines resulting in diazonium salts. It is an electrophilic substitution, with nitrosyl ion, NO⁺, as substituent, which can be furnished either as such or in bound form attached to a Brønsted base. The possible or actual carriers of NO⁺ in N-nitrosation are the following

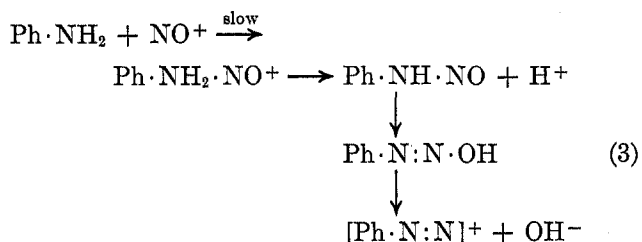
NO⁺, NO·OH₂⁺, NO·X,

NO·NO₃, NO·NO₂, NO·OH (1)

arranged in order of increasing basic strength of the combined base. The nitrosating agents are usually formed from nitrous acid, and the overall reaction of diazotization in an actual experiment can be formulated, for example, as



where X represents a halogen. An excess of acid is necessary to prevent the formation of diazotates from the diazonium ion [PhN₂]⁺. Assuming the nitrosating agent has been supplied, then the first (rate-determining) step of diazotization is the attack of the agent on the lone-pair electrons of the primary amine followed by a sequence of fast steps ending in diazonium ion.



In water as the reaction medium, the first five species of (1) are the actual nitrosating agents. Accordingly, the reaction rate equation contains five terms or less depending on experimental conditions. In methanol, NO·OH₂⁺ is replaced by NO·CH₃OH⁺ (solvated nitrosyl ion or protonated methyl nitrite), and the only actual agent is NO·X. Using aniline and hydrochloric acid as two of the reactants, the reaction rate in methanol can be expressed according to Schmid and Muhr by the simple equation³

$$v = \frac{d(\text{PhN}_2^+)}{dt} = k_0 f_{\text{HCl}}^2 [\text{PhNH}_3^+] [\text{CH}_3\text{ONO}] [\text{Cl}^-] \quad (4)$$

with parentheses symbolizing total and the brackets real concentrations, respectively. *k*₀ is a reaction rate coefficient and *f*_{HCl} is the mean activity coefficient of HCl.

By changing solvent from water to methanol, the reaction mechanism and the rate expression simplify drastically. Although the chemical properties of the two solvents are related to a certain extent, their dielectric constants *D* differ substantially (*D*_{H₂O}^{20°} = 80.36, *D*_{CH₃OH}^{20°} = 33.73). In the present work a systematic study has been performed on the effect of changing dielectric constant on reaction rate and mechanism of diazotization. Also, the effect of extreme changes of reaction medium, *e.g.*, using an aprotic solvent, has been investigated. A series of methanol-carbon tetrachloride mixtures was chosen as solvent

(1) (a) This article is based upon the doctoral dissertation presented to the faculty of Vienna Technical University in 1967. Also presented in part at the 24th Northwest Regional Meeting of the American Chemical Society in Salt Lake City, Utah, June 1969. (b) Correspondence should be addressed to Department of Chemistry, The University of Georgia, Athens, Ga. 30601.

(2) Cf. the review article by H. Schmid, *Chem.-Ztg.*, *Chem. App.*, **86**, 809 (1962), and references cited therein; E. D. Hughes, C. K. Ingold, and J. H. Ridd, *J. Chem. Soc.*, 58 (1958).

(3) H. Schmid and G. Muhr, *Monatsh. Chem.*, **93**, 102 (1962).

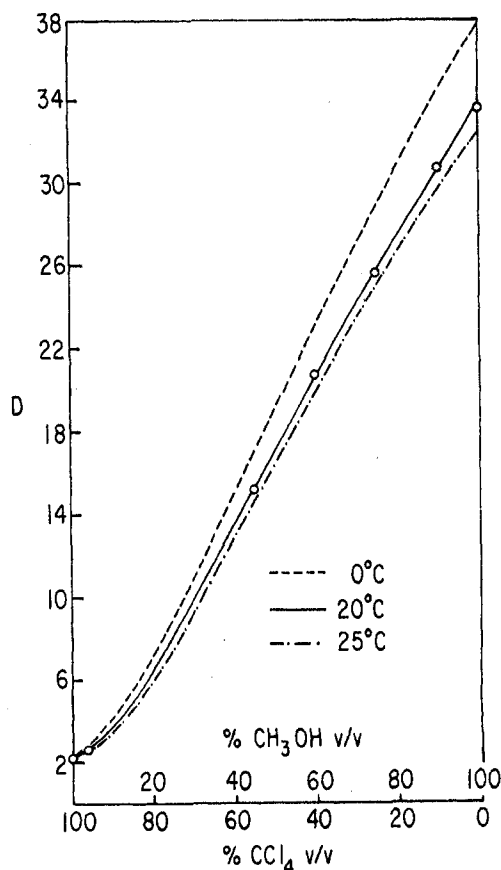


Figure 1. Dielectric constant of the methanol-carbon tetrachloride system at different temperatures.

for this purpose, instead of using several solvents, possibly with quite different chemical properties. The advantages of this system are based on the fact that CH_3OH and CCl_4 are miscible in all proportions. Thus, the dielectric constant of the mixture is variable continuously over a wide range (Figure 1). Consequently, any continuous monotonic function with the general form

$$\Psi = f(D) = F(\text{composition of the mixture}) \quad (5)$$

can be accurately interpolated between a few data points, if Ψ is property of a substance or chemical system dissolved in the mixture. Since CCl_4 can be regarded inert even against NOCl , it acts only as an indifferent diluent, and the chemical properties of the solvent determined by the component methanol are retained for any composition of the mixture (excluding pure CCl_4). In addition, since the composition of the mixtures lies between pure methanol and carbon tetrachloride, one may compare the kinetics in a medium already studied (pure methanol) with those in an aprotic solvent.

Experimental Section

A. Chemicals. All reagents used were analytical grade (purchased from Merck or Riedel de Haën) or

were purified by conventional methods. The concentration of the methanolic NaNO_2 solution was checked according to Fischer.⁴ NOCl was obtained from the Matheson Co., analyzed by the Addison-Thompson method,⁵ and purified from N_2O_4 with potassium chloride.⁶ The concentration of NOCl in pure CCl_4 has been determined by oxidation-reduction titrations. The methanolic HNO_3 was prepared by titration of a methanolic AgNO_3 solution with methanolic HCl with cooling and excluding light. *p*-Hydroxyazobenzene was prepared by Oddo and Puxeddu's method.⁷

B. Apparatus. The dielectric constants were measured at 20° by using Dipolmeter WTW Type DM Ol, and D values for other temperatures were obtained through linear extrapolation by using literature data.⁸ The optical density data were obtained on a Zeiss Spektralphotometer PMQ II. The temperature was controlled to $\pm 0.05^\circ$ with an Ultra Kryostat UK 30.

C. Kinetic Experiments. The reactions were initiated by rapid mixing of two thermostated solutions resulting in a 100-ml reaction mixture. One of the two solutions contained aniline, acid (HCl or HNO_3), and in some cases NaCl and/or NaClO_4 , and the other NaNO_2 or NOCl , respectively. The progress of diazotization has been followed by extracting samples from the reaction mixture and determining the diazonium ion concentration colorimetrically. Reaction in the extracted samples was quenched with the same volume of a strong alkaline methanolic phenol solution with a large excess of phenol. This quenching produces instantaneous formation of *p*-hydroxyazobenzene with theoretical yield with respect to the diazonium ion concentration. The optical density of these solutions was measured at the wavelength of the absorption maximum of the dye (λ_{max} 400 $\text{m}\mu$) and concentrations were obtained from the linear calibration curve. The molar decadic absorptivity of the dye ($\epsilon_{\text{max}}^{20^\circ} = 2.748 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) was determined to be independent of the composition of the reaction mixture after quenching, ranging from pure methanol to 50% CCl_4 v/v.

In long runs, the amount of diazonium ions produced and detected did not reach the theoretical yield (Figure 2), owing to slow decomposition of nitrous acid and diazonium ions and to side reactions of the latter. The two conceivable significant side reactions of diazonium ions are their hydrolysis and their N-coupling with unchanged amines to give diazoamino compounds. To eliminate these possible systematic errors the initial reaction rates v_0 have been determined throughout in

(4) W. M. Fischer, *Z. Anorg. Allg. Chem.*, **78**, 134 (1912).

(5) C. C. Addison and R. Thompson, *J. Chem. Soc.*, 218 (1949).

(6) C. W. Wittaker, F. O. Lundstrom, and A. R. Merz, *Ind. Eng. Chem.*, **23**, 1410 (1931).

(7) G. Oddo and E. Puxeddu, *Chem. Ber.*, **38**, 2755 (1905).

(8) "Handbook of Chemistry and Physics," 44th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1963, p 2613; Landolt-Börnstein, "Zahlenwerte und Funktionen," Vol. 2, Part 6, 6th ed, Springer-Verlag, Berlin, 1959, p 632.

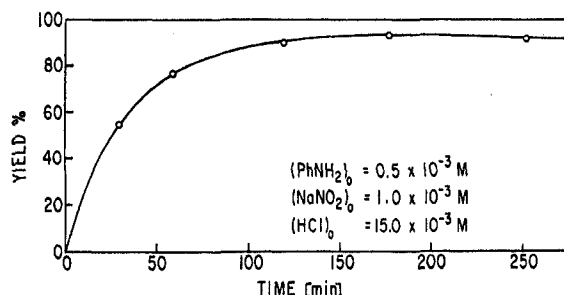


Figure 2. Yield of diazonium ion (as *p*-hydroxyazobenzene) vs. time in a typical long run.

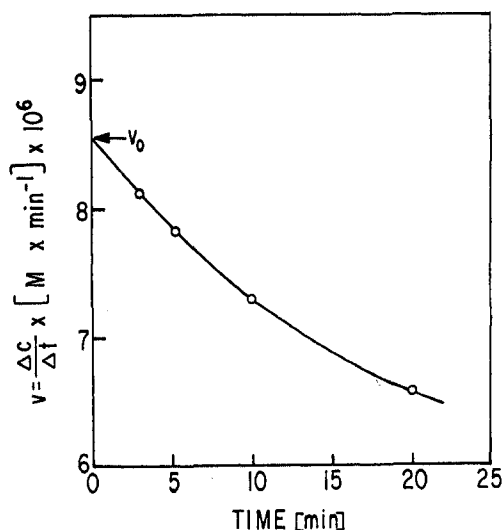


Figure 3. Example for the graphical determination of the initial reaction rate v_0 .

this work by extrapolating the measured average rates to time zero (Figure 3).

Results and Discussion

A. Most of the kinetic experiments have been done in $\text{CH}_3\text{OH}-\text{CCl}_4$ mixtures 1:1 by volume, at 0° . The order of reaction with respect to the different reactants and to the ionic strength $I = \frac{1}{2} \sum z_i^2 c_i$ has been determined by the van't Hoff method. Varying successively the initial concentration c_0 of each component and keeping all other parameters constant at the same time, the slopes of the curves $\log v_0$ vs. $\log c_0$ (Figure 4) give the order with respect to each component. Varying the initial concentration of aniline, sodium nitrite, hydrochloric acid, and the initial ionic strength (Figure 4), one obtains the proportionality

$$v_0 \propto (\text{PhNH}_2)_0 (\text{NaNO}_2)_0 (\text{HCl})_0^x I^y \quad (6)$$

where $0.365 \geq x \geq 0.098$ and $-1.394 \leq y \leq -0.311$, the latter indicating negative salt effects. Varying $(\text{Cl}^-)_0$ and $(\text{H}^+)_0$ (Figure 4) instead of $(\text{HCl})_0$, the proportionality (6) can be replaced by

$$v_0 \propto (\text{PhNH}_2)_0 (\text{NaNO}_2)_0 (\text{Cl}^-)_0 (\text{H}^+)_0^z I^y \quad (7)$$

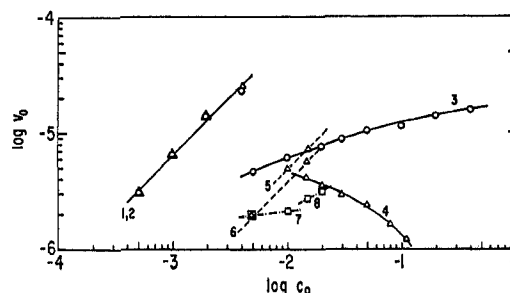


Figure 4. Determination of the order of reaction with respect to the reactants: curve 1, PhNH_2 ; 2, NaNO_2 ; 3, HCl ; 4, I ; 5 and 6, Cl^- ; and 7 and 8, H^+ .

where $0 < z < 1$, indicating protonic catalysis not found in pure methanol.³

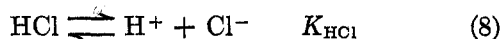
Now let us consider some aspects of the experimental technique used in pure methanol, as well as in the present work. The variation of the initial concentration of a single component, say chloride ion, at a time can be achieved with the usual balancing-of-concentrations method only if values of the degree of dissociation α of electrolytes present in the reaction mixture are known or if all values of α are equal. The knowledge of α is indispensable also for the calculation of ionic concentrations and activity coefficients. A complete dissociation of all electrolytes was assumed in methanol.³ This assumption is, however, unjustified, since for all electrolytes in solvents of lower dielectric constant, dissociation is incomplete at accessible concentrations.⁹ The degrees of dissociation of HCl , NaCl , and NaClO_4 at 0° in pure methanol and in $\text{CH}_3\text{OH}-\text{CCl}_4$ mixture (1:1 by volume) have been estimated based on conductance measurements,¹⁰ where each electrolyte was alone in the solution under its own ionic strength. Values of α have been found to deviate substantially from each other and from unity in methanol. In the $\text{CH}_3\text{OH}-\text{CCl}_4$ mixture ($D_0 = 19.1$) dissociation is ever more incomplete; however, the α values for all three electrolytes are equal (the maximum deviation is less than 0.02) and are approximately constant ($\alpha = 0.6 \pm 0.02$) within the range of ionic strength 1.55×10^{-3} to $3.35 \times 10^{-2} M$. Since no information is available about the degree of ionization of $\text{PhNH}_3^+\text{Cl}^-$, it has been assumed to be the same as that of HCl , NaCl , and NaClO_4 . Failure to consider incomplete dissociation in methanol may account for the fact that no H^+ catalysis was detected in this solvent.

B. *Mechanism and Rate Equation.* To be able to postulate a reaction mechanism which is in accord with the empirical rate expression 7, consider all preliminary reactions which have gone to completion or

(9) R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, **55**, 476 (1933).

(10) Z. A. Schelly, Dissertation, Vienna Technical University, 1967.

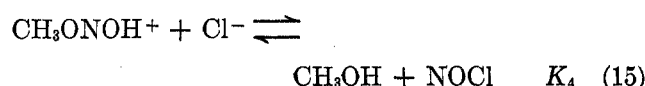
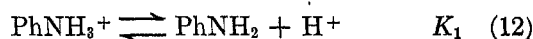
have attained their equilibrium positions, respectively, at zero time. Because of the large excess of methanol,



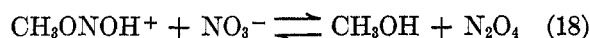
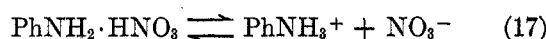
reactions 9 and 10 are very fast and complete, so that

$$(\text{NaNO}_2)_0 \simeq [\text{CH}_3\text{ONO}]_0 \quad (11)$$

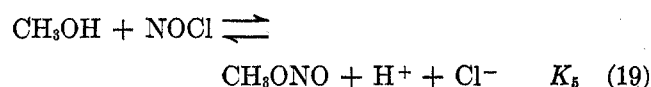
In addition, we have the equilibria



The equilibria 8, 13, and 15 are replaced by

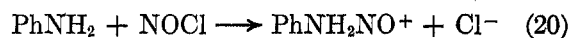


if HNO_3 is used instead of HCl and no Cl^- ions are present in the mixture. However, no diazotization occurs in the absence of halogen ions, indicating that CH_3ONOH^+ and N_2O_4 do not N-nitrosate aniline, unlike their action in water. The equations for equilibria 14 and 15 may be combined so that



where $K_5 = (K_3 \times K_4)^{-1}$.

Based on expression 7, the actual diazotizing agent must be a species, for which the real concentration increases with increasing $(\text{NaNO}_2)_0$, $(\text{Cl}^-)_0$, and $(\text{H}^+)_0$. Indeed, in such a case, equilibria 14 and 15 will be shifted in a direction favoring the formation of NOCl . Thus, one can postulate the rate-determining step as being the same as in pure methanol,³ followed by



fast steps given in eq 3. This results in the reaction rate equation

$$v = k[\text{PhNH}_2][\text{NOCl}]f_{\text{PhNH}_2}f_{\text{NOCl}}/f_{\pm} \quad (21)$$

where k is a rate constant and f_{\pm} is the activity coefficient of the activated complex. Considering that

$$(\text{PhNH}_2) = [\text{PhNH}_2] + [\text{PhNH}_3^+] + [\text{PhNH}_2 \cdot \text{HCl}] \quad (22)$$

$[\text{NOCl}]$ can be calculated from equilibrium 19, and the real concentrations in eq 22 from the equilibria 12 and 13, respectively. Substituting the calculated

values into eq 21, and (a) equating the activity coefficients of nonelectrolytes to unity, (b) neglecting the dependence of the activity coefficients of electrolytes on their ionic radii, and (c) symbolizing $f_{\text{H}^+} \times f_{\text{Cl}^-}$ by f_{HCl}^2 , one obtains the rate equation

$$v = kK_5^{-1}a_{\text{CH}_3\text{OH}}^{-1} \frac{K_1[\text{H}^+][\text{Cl}^-]}{K_1 + [\text{H}^+] + \frac{1}{K_2}[\text{H}^+][\text{Cl}^-]f_{\text{HCl}}^2} \times (\text{PhNH}_2)[\text{CH}_3\text{ONO}]f_{\text{HCl}}^2 \quad (23)$$

where $a_{\text{CH}_3\text{OH}}$ is the activity of methanol. Equation 23 follows automatically from the proposed mechanism. It is compatible with the empirical rate law 7, if one transforms the latter, accounting for the incomplete dissociation of the electrolytes, and utilizing eq 11

$$v \propto [\text{H}^+]^{z'}[\text{Cl}^-]^w(\text{PhNH}_2)_0[\text{CH}_3\text{ONO}]I^{v'} \quad (24)$$

Now $0.8 \leq w \leq 0.9$ and $0.082 \leq z' \leq 0.22$.

Comparing eq 4 and 23, it is obvious that k_0 in (4) is further resolvable, thus

$$k_0[\text{PhNH}_3^+] = kK_5^{-1}a_{\text{CH}_3\text{OH}}^{-1} \times \frac{K_1[\text{H}^+](\text{PhNH}_2)}{K_1 + [\text{H}^+] + \frac{1}{K_2}[\text{H}^+][\text{Cl}^-]f_{\text{HCl}}^2} \quad (25)$$

Since the thermodynamic equilibrium constants K_1 , K_2 , and K_5 at 0° in eq 23 are not known, the rate constant k cannot be calculated. Hence, instead of k the coefficients k' and k'' given by

$$k' = kK_5^{-1} \frac{K_1}{K_1 + [\text{H}^+] + \frac{1}{K_2}[\text{H}^+][\text{Cl}^-]f_{\text{HCl}}^2} \quad (26)$$

$$k'' = k'[\text{H}^+] \quad (27)$$

have been calculated and plotted vs. I (Figure 5). k' is approximately constant at $I > 0.035 M$, in comparison with k'' , which can be considered constant only at very small ionic strength where $I < 0.0125 M$.

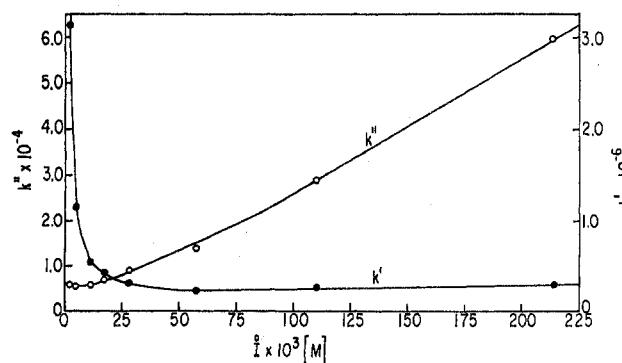


Figure 5. k' and k'' vs. the ionic strength I .

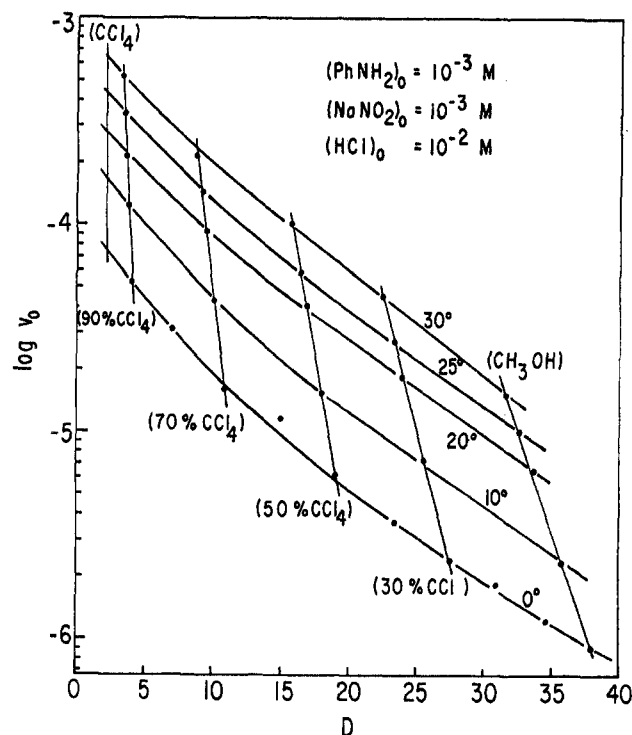


Figure 6. $\log v_0$ vs. D at different temperatures.

C. *Variation of the Temperature and the Composition of the Solvent.* In these experiments the initial concentrations of all reactants were kept constant, and only the temperature or the dielectric constant of the medium was varied (Figure 6). With decreasing polarity of the solvent the reaction rate shows a steep increase. There are several arguments that would predict the opposite result. (1) The activity coefficients fall with decreasing D of the solvent, which should lead to a smaller rate (cf. eq 21). (2) If the activated complex is more polar than the reactants, the rate constant k should decrease with the D value of the medium.¹¹ The activated complex in the present case is certainly more polar than the reactants since the products are ionic (see eq 20). (3) The activation energy in an ionization reaction does not change rapidly from solvent to solvent; however, the entropy of activation is always negative and becomes more negative as the polarity of the solvent decreases. Thus the rate of reaction should increase with the polarity of the solvent.¹² (4) The preliminary equilibria 8, 12,¹³ and 13 are shifted with decreasing D in favor of association of the species, tending to diminish $[\text{PhNH}_2]$ and $[\text{NOCl}]$, which also should lead to a smaller rate.

However, all these effects (1 through 4) are overwhelmed by the enhancement of the reaction rate caused by the decrease of the activity of methanol, $a_{\text{CH}_3\text{OH}}$ (see eq 23), and by the displacement of equilibrium 19 in favor of higher NOCl concentration, in accord with decreasing dielectric constant of the medium. Also the weaker solvation of the reactants

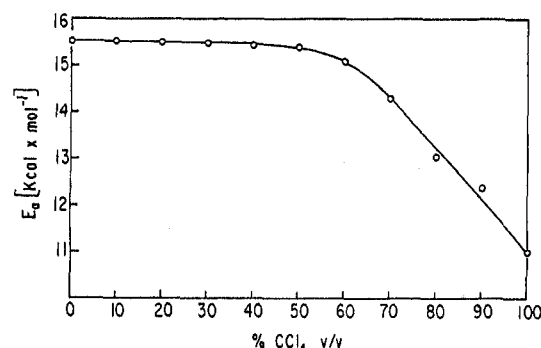


Figure 7. The activation energy E_a vs. composition of the solvent.

amine and NOCl with decreasing polarity of the solvent contributes to the increase of the reaction rate.

D. *Activation Energy.* The calculated activation energies are plotted vs. composition of the solvent in Figure 7. The insensitivity of the activation energy E_a to the dielectric constant of the medium, in the range between pure methanol and 60% CCl_4 v/v, is a further support for the proposed mechanism, since this property of the activation energy is characteristic for reactions producing ions. If the medium contains more than 60% CCl_4 v/v, E_a decreases significantly because the reactants are less solvated since methanol is not present at sufficient concentration, and/or another step producing no ions becomes rate controlling. If the latter is the case, this step is presumably the rearrangement of the nitrosamine $\text{Ph}\cdot\text{NH}\cdot\text{NO} \rightarrow \text{Ph}\cdot\text{N}:\text{N}\cdot\text{OH}$ (cf. eq 3), probably involving the protonation and subsequent deprotonation of the solvent. With decreasing methanol content of the medium the proton transfer becomes more and more difficult. By choosing the right experimental conditions¹⁴ the tautomerization can be slowed down to such an extent that diazotization practically stops at the nitrosamine stage. Consequently, rate eq 23 is valid with certainty only up to 60% CCl_4 v/v in accord with the mechanism proposed for pure methanol as solvent, and confirmed in $\text{CH}_3\text{OH}-\text{CCl}_4$ mixture, 1:1 by volume.

E. The diazotization of aniline with NOCl in pure carbon tetrachloride¹⁵ results in a heterogeneous mixture, because all polar products such as $[\text{PhN}_2]^+\text{Cl}^-$,

(11) Cf. A. A. Frost and R. F. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1965, p 140.

(12) Reference 11, p 137.

(13) K_1 of equilibrium 12 decreases with decreasing polarity of the solvent; e.g., in water at 0° $K_1 = 7.5 \times 10^{-5}$ (K. J. Pedersen, *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.*, **14**, 9 (1937); **15**, 3 (1937)) in comparison with $K_1 = 3 \times 10^{-7}$ in methanol at 2° (H. Schmid, A. Maschka, and W. Melhardt, *Monatsh. Chem.*, **99**, 443 (1968)).

(14) PhNHNO as intermediate in diazotization was proved in ethyl ether at -78° by its uv spectrum by E. Müller and H. Haiss, *Chem. Ber.*, **96**, 570 (1963). Under such experimental conditions the nitrosamine can be preserved for days.

(15) On the diazotization of aniline with NOCl in ethyl ether, cf. E. Bamberger, *Chem. Ber.*, **27**, 668 (1894).

$\text{PhNH}_2 \cdot \text{HCl}$, and H_2O precipitate instantaneously, excluding the applicability of homogeneous kinetics. In such a case, one has to account also for transport phenomena and for the development of new phases and interfaces. However, by extrapolating the results obtained in $\text{CH}_3\text{OH}-\text{CCl}_4$ mixtures, where no precipitation occurs, one can readily obtain rate data (v_0) for 100% CCl_4 as medium (Figure 6). This is possible since all reaction rates determined in the mixtures, as

well as the values obtained for CCl_4 are initial rates, and at time zero diazotization is, even in a medium with $D_0 = 2.291$, a homogeneous reaction.

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The Reduction of Ruthenium(III) Hexaammine by Hydrogen Atoms and Monovalent Zinc, Cadmium, and Nickel Ions in Aqueous Solutions

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The specific rates of reaction of H atoms, Zn^+ , Cd^+ , and Ni^+ with $\text{Ru}(\text{NH}_3)_6^{3+}$ were determined. The mechanism of reduction of hexaammine complexes by hydrogen atoms is discussed. It is suggested that hydrogen atoms might penetrate the ligand sphere and form a seven coordinated transition state. The redox potentials of the $\text{Zn}^+/\text{Zn}^{2+}$ and $\text{Cd}^+/\text{Cd}^{2+}$ couples are estimated as being equal to 2.0 ± 0.4 and 1.8 ± 0.4 V, respectively.

The specific rates of the reactions of hydrogen atoms,²⁻⁴ monovalent zinc, cadmium, and nickel ions,⁵ and hydrated electrons^{5,6} with a series of cobalt(III) complexes have been measured recently. It was found that the reactions of e_{aq}^- with all of these complexes are diffusion controlled. However, for the other strong reducing agents, many of the reactions are slower than diffusion controlled and the trend of reactivity toward the different complexes is similar to that found for the much slower reactions by mild reducing agents, *e.g.*, Cr^{2+} , $\text{Ru}(\text{NH}_3)_6^{2+}$, and V^{2+} . The results were interpreted as indicating that whereas hydrogen atoms react only *via* the inner-sphere mechanism,²⁻⁴ the monovalent ions have varying mechanisms, being outer sphere for Zn^+ and mostly inner sphere for Cd^+ and Ni^+ . Hydrogen atoms are expected to react always *via* the inner-sphere mechanism as a reaction *via* the outer-sphere mechanism would yield either the non-hydrated H^+ ion and therefore be an endothermic process or require a very high free energy of activation in order to obtain the hydrogen atoms in the configuration of the hydronium ions. However, it was found that H atoms react readily with $\text{Co}(\text{NH}_3)_6^{3+}$,^{2,3} though it is

generally agreed that the latter complex can be reduced only *via* the outer-sphere mechanism.⁷

With the hope of obtaining more information on the mechanism of reduction of hexaammine complexes by strong reducing agents, the specific rates of reaction of $\text{Ru}(\text{NH}_3)_6^{3+}$ with H atoms, Zn^+ , Cd^+ , and Ni^+ have been measured. The choice of this complex ion was made because its reduced form, while having nuclear configuration similar to the analogous cobalt complex, has a completely different structure, having low spin configuration and no electrons in the e_g orbitals. Reduction of this complex by Cr^{2+} and V^{2+} have been recently measured.^{8,9}

(1) To whom correspondence should be addressed.

(2) G. Navon and G. Stein, *J. Phys. Chem.*, **69**, 1390 (1965).

(3) M. Anbar and D. Meyerstein, *Nature*, **206**, 816 (1965).

(4) J. Halpern and T. Rabani, *J. Amer. Chem. Soc.*, **88**, 699 (1966).

(5) D. Meyerstein and W. A. Mulac, *J. Phys. Chem.*, **73**, 1091 (1969).

(6) The specific rates of reaction with e_{aq}^- are tabulated in M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotopes*, **18**, 493 (1967).

(7) H. Taube and E. S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969).

(8) J. E. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1686 (1964).