When it was heated at 110–115° for thirty minutes, no changes resulted and the melting point was the same. The substance, therefore, is the Δ^2-pyrazoline. In an experiment duplicating the one above, except that the temperature was maintained at -14 to $-15°$ throughout, a small amount of white crystals suddenly formed after the solution had stood for forty-five minutes. No apparent increase in the amount of solid was observed after two hours; the solid (about 0.1 g.) was then removed from the ethereal solution. This white solid melted at 90–92°, and immediately resolidified to a yellow material which then melted at 98–100°. The main part of the reaction product, isolated later, was crystallized from methanol. It was white and melted at 100.5–101°. Complete removal of the solvent under reduced pressure caused a part of the material to be transformed into the yellow form. The white and yellow crystals were separated mechanically; both melted at 100.5–101°. The material in the melting point tube always solidified to a yellow crystalline solid, regardless of whether the initial material was white or yellow. Rapid or slow melting of the white solid did not change the melting point, and the transformation which occurred at 90–92° was never observed again.

Oxime.—This was prepared in the usual way; after one crystallization from aqueous ethanol it melted at 181° in agreement with Azzarello's report of 181–182°.

Pyrolysis of I.—The pyrazoline I (6.75 g.) was heated at 190–205° under 16–20 mm. for two hours in an apparatus arranged for distillation. The distillate, consisting of an oil and some solid (I), was transferred to a Claisen flask and distilled under reduced pressure in an atmosphere of nitrogen. The fraction boiling at 132–138° under 17 mm. (2.77 g., 46%) had $n^{25}\text{D}$ 1.5662 and was β-methylacetophenone. The ketone decolorized a solution of potassium permanganate in acetone and it readily added bromine.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.50; H, 7.50. Found: C, 81.96; H, 7.40.

Under atmospheric pressure, decomposition of the pyrazoline began at 135°, and was very rapid at 230–235°. After thirty minutes at this temperature, the material yielded only 7.5% of the ketone.

Semicarbazone.—This was prepared in the usual way and recrystallized three times from aqueous ethanol. It then melted at 183.5–184°.

Anal. Calcd. for $C_{12}H_{15}ON_3$: C, 66.36; H, 6.91. Found: C, 66.21; H, 6.87.

Ozonolysis.—A stream of ozonized oxygen was passed for ten minutes through a cooled solution of β-methylbenzalacetone (0.618 g., 0.0037 mole) in chloroform (22 cc.). The solvent was removed from the colorless solution under reduced pressure at room temperature, and the residual ozonide was reductively cleaved by boiling it for forty-five minutes with water (50 cc.), zinc (3 g.), a small crystal each of silver nitrate and hydroquinone.[5] The mixture was steam distilled and the distillate was extracted with ether. Evaporation of the ether left a residue of light colored oil (3 or 4 drops) which was identified as acetophenone by preparation of the phenylhydrazone (m. p. 97–98°) and the semicarbazone (m. p. 194.5–195°) and comparison of these with authentic specimens.

Summary

1. The product obtained by the reaction of benzalacetone and diazomethane is Δ^2-3-aceto-4-phenylpyrazoline, and Azzarello's work has been confirmed. Evidence was obtained that the Δ^1-pyrazoline, is actually formed first, but that it is extremely labile and changes rapidly into the Δ^2-isomer

2. This pyrazoline was pyrolyzed and β-methylbenzalacetone was identified as the chief product of the decomposition. No cyclopropane derivative was isolated.

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[5] Whitmore and Church, This Journal, **54**, 3710 (1932); Church, Whitmore and McGrew, *ibid.*, **56**, 176 (1934).

MINNEAPOLIS, MINNESOTA RECEIVED OCTOBER 26, 1942

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MARYLAND]

The Rate of Conversion of Ammonium Cyanate to Urea in Non-aqueous Solvents. VI[1]

BY W. J. SVIRBELY AND SELMER PETERSON[2,3]

The rate of conversion of ammonium cyanate to urea in five non-aqueous solvents over a 30° temperature range is reported in this research. The previous papers[4] of this series were concerned with studying the reaction in various solvent–water mixtures over a 30° temperature range and at various constant dielectric constants. It was considered worth while to study the reaction in one-component solvents at varying dielectric constant. The reaction was carried out in methanol, ethanol, isopropanol, ethylene glycol and glycerol. Calculations based on the experimental data are compared with those obtained from existing solution kinetic theories.

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[1] Presented at the Buffalo meeting of the A. C. S., September, 1942.

[2] Part of a thesis submitted by Selmer Peterson to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Present address: Mellon Institute of Industrial Research, Pittsburgh, Pa.

[4] Svirbely and Lander, This Journal, **61**, 3538 (1939), was the last paper of the series.

Materials and Experimental Procedures

Silver cyanate was prepared as previously described.[4] A solution of potassium thiocyanate (0.0200 molar) was prepared from C. P. analytical grade salt. A solution of silver nitrate (0.0280 molar) was prepared from fused C. P. silver nitrate. The strengths of both solutions were checked against pure sodium chloride. The $AgNO_3$/KCNS ratio was checked every day and the value obtained was used in the experiments carried out during the day.

The indicator solution was prepared by saturating 3 molar nitric acid with C. P. ferric nitrate or alternatively by saturating 3 molar nitric acid with C. P. ferric ammonium sulfate.

Absolute methanol was fractionally distilled, refluxed over sodium and again fractionated, collecting the middle 80%. The entire sample distilled at a constant temperature and had a refractive index of 1.3280 at 22°.

Absolute ethanol was treated as above. The purified material had a refractive index of 1.3573 at 32°.

Isopropanol was purified by two fractional distillations. The collected sample had a refractive index of 1.3758 at 24°.

Ethylene glycol was dried over sodium sulfate for several weeks and then vacuum distilled, collecting the middle 80%. The middle fraction was fractionally distilled and the sample collected had a refractive index of 1.4292 at 24°.

Glycerol was dried by heating Baker C. P. analyzed glycerol slowly at 180°. The refractive index of the resulting material was 1.4731 at 20°.

All refractive indices given above agree within ±0.0002 with literature values after reducing them to 20°.

All reactions were carried out in a thermostat held within ±0.02°. The thermometer was calibrated against a Bureau of Standards calibrated thermometer. All pipets and burets used in the analytical method were carefully calibrated.

In conducting an experiment in methanol, ammonium chloride calculated to give an ammonium ion concentration of about 0.07 *M* was weighed out and added to 130 ml. of methanol. The solution was stirred, precautions being taken to keep out moisture. After dissolving, excess silver cyanate was added and agitation continued until the solution was free of chloride ion. The flask and its contents were then cooled in ice to slow down the conversion of ammonium cyanate. The solution was filtered; the filtrate was heated to approximately the thermostat temperature over an open flame and placed in the thermostat. After the establishment of temperature equilibrium, an initial sample (10 ml. approx.) was withdrawn and pipetted into a weighed flask containing a known excess of standard silver nitrate. The flask and contents were weighed, the solution was filtered to remove the precipitated silver cyanate, and the flask and precipitate were carefully washed with several portions of ice-water. Five ml. of 6 *M* nitric acid and 1 ml. of indicator solution were added to the filtrate and the filtrate was titrated with standard potassium thiocyanate to determine the excess silver ion. As the reaction proceeded, numerous samples were treated similarly. The method of weighing to determine the amount of added reaction mixture was found to be more acceptable than the volumetric procedure used in the earlier papers. The volume of the sample is easily calculated from the weight data using the density of the pure solvent at the specified temperature. Densities taken from the "I. C. T." were used in the calculations.

In conducting an experiment in ethanol, the experimental method was slightly modified due to the lower solubility of ammonium chloride in ethanol. The silver cyanate was added while solid ammonium chloride was still present. Agitation for approximately fifteen minutes allowed all of the ammonium chloride to be used up since the reaction forming silver chloride quickly reduces the ammonium chloride concentration so that the undissolved material can go into solution.

In conducting an experiment in isopropanol it was found necessary to heat the isopropanol to 50°. The ammonium chloride and excess silver cyanate were added and the mixture agitated for about twenty minutes while maintaining the temperature of 50°. The mixture was then cooled in ice before filtration and the procedure described previously was applied.

In conducting an experiment in ethylene glycol, it was found necessary to use suction filtration with a tight paper (No. 50) in order to prepare the ammonium cyanate solution. Otherwise the method was the same as in methanol.

In conducting an experiment in glycerol, due to solubility difficulties and to the high viscosity of the solvent, a different procedure for preparing the ammonium cyanate solution was resorted to. Cyanuric acid was prepared[5a] by heating urea at 220° with twice its weight of zinc chloride, decomposing the solid mass with hydrochloric acid after cooling and recrystallizing the acid from hot water. Solid ammonium cyanate was prepared[5b] by passing ammonia into a cold ethereal solution containing cyanic acid which was obtained by heating the cyanuric acid. All tests run on the ammonium cyanate agreed with those of Walker and Wood. The solid ammonium cyanate was dissolved in glycerol, the solution was heated to approximately the thermostat temperature and was then placed in the thermostat until temperature equilibrium was established before removing a sample. The filtration and analysis operations after removing a sample have already been described.

Experimental Results

Average values of the limiting velocity constant at $\mu = 0$ listed in Table I were obtained by means of the usual equation[9b]

$$k_0t = \left(\frac{1 + 4A\sqrt{C}}{C}\right) - \left(\frac{1 + 4A\sqrt{C^0}}{C^0}\right) \qquad (1)$$

Each value of k_0 recorded in Table I is the mean of at least two duplicate runs,[6] from five to nine separate observations being made for each run. In the worst case duplicate k_0 values, obtained from separate runs, agreed within 4.2%. The usual agreement was considerably better than that and in the average case k_0 values from duplicate runs agreed within about 0.5%.

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(5) (a) R. Von Walther, *Chem. Abs.*, **3**, 2141 (1909); (b) Walker and Wood, *J. Chem. Soc.*, **77**, 21 (1900).

(6) Excepting the runs in glycerol at 60 and 70°. Only one run was made in each case.

TABLE I

SUMMARY OF DATA AT ZERO IONIC STRENGTH IN NON-AQUEOUS SOLVENTS

Temp., °C.	k_0 values in									
	Methanol		Ethanol		Isopropanol		Glycol		Glycerol	
	Eq. 1	Eq. 3	Eq. 1	Eq. 3	Eq. 1	Eq. 3	Eq. 1	Eq. 3	Eq. 1	Eq. 3
20	0.0772	0.0783	0.197	0.198	0.183	0.184				
30	.270	.274	.596	.594	.597	.605	0.0542	0.0544		(0.0437[a])
40	.876	.885	1.69	1.69	1.84	1.84	.180	.187	0.151	.152
50	2.67	2.68	4.49	4.48	5.26	5.27	.598	.597		(.490[a])
60							1.80	1.80	1.50	1.45
70									4.02	4.04
B (eq. 3)	15.46		13.93		14.98		15.62		15.50	
E (eq. 3)	22,250		19,650		21,100		23,440		23,400	

[a] Calculated from data obtained at the other temperatures.

TABLE II

SUMMARY OF DATA AT $\sqrt{\mu} = 0.194$ IN NON-AQUEOUS SOLVENTS

Temp., °C.	k_1 values in									
	Methanol		Ethanol		Isopropanol		Glycol		Glycerol	
	Eq. 2	Eq. 3	Eq. 2	Eq. 3	Eq. 2	Eq. 3	Eq. 2	Eq. 3	Eq. 2	Eq. 3
20	0.0282	0.0280	0.0550	0.0555	0.0365	0.0362				
30	.0960	.0957	.161	.163	.114	.113	0.0228	0.0226		
40	.305	.303	.445	.446	.336	.329	.0745	.0765	0.0665	0.0658
50	.908	.902	1.14	1.15	.911	.903	.243	.241		
60							.719	.712	.616	.609
70									1.69	1.67
B (eq. 3)	14.72		12.97		13.64		15.00		14.90	
E (eq. 3)	21,850		19,100		20,250		23,110		23,060	
E (eq. 5)	22,130		19,440		20,690		23,360		23,330	

Values of the velocity constant k_1 at $\sqrt{\mu} = 0.194$ obtained from k_0 by the relation[4]

$$k_1 = \frac{k_0}{1 + 2A\sqrt{\mu}} \tag{2}$$

are listed in Table II. The linear plots obtained on plotting both log k_0 and log k_1 against $1/T$ in the five solvents can be expressed by means of the general equation

$$\log k = B - E/4.587T \tag{3}$$

Values of the frequency factor B and of the energy of activation E for the reaction in the various solvents at both zero ionic strength and at $\sqrt{\mu} = 0.194$ are listed in Tables I and II, respectively.

Values of k_1 were determined in a few cases selected at random by using the method of Warner and Stitt.[7] The reciprocal of the ammonium ion concentration was plotted against the time (minutes). The slope of the curve at $\sqrt{\mu} = 0.194$ was determined and the corresponding value of k_1 was calculated from it. Table III gives a comparison of the two methods used. It is obvious that equations 1 and 2 are quite satisfactory for calculating velocity constants within the limit of experimental error and their use in non-aqueous solvents justified.

TABLE III

Solvent	t, °C.	k_1 (graphical)	k_1 (calcd. by eq. 2)
Glycol	50	0.246	0.243
Glycol	60	.720	.718
Ethanol	30	.162	.162
Methanol	20	.0276	.0280

Discussion

Deviations from the linearity predicted by Scatchard's[8] equation

$$\log k_0 - \log k_0^* = \frac{e^2 Z_A Z_B}{2.3KTr}\left(\frac{1}{D^0} - \frac{1}{D}\right) \tag{4}$$

have been observed[4,9] in this reaction and in others. Salting out of the less polarizable component of a two-component mixture by the ion, thereby giving around the ion a higher concentration of the more polarizable component, has been advanced as a possible answer for the deviations. For the various solvent–water mixtures previously used in studying the ammonium cyanate reaction, this means that in every case there should have been an increase in the concentration of water molecules around the ions. Recently it has been pointed out[10] that if the salting out of the less polarizable component is the answer for the deviations from linearity,

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(7) Warner and Stitt, THIS JOURNAL, **55**, 4807 (1933).

(8) Scatchard, *Chem. Rev.*, **10**, 229 (1932).

(9) (a) La Mer, *J. Franklin Inst.*, **225**, 709 (1938); (b) Warner and Warrick, THIS JOURNAL, **57**, 1491 (1935).

(10) Scatchard, *J. Chem. Phys.*, **7**, 660 (1939).

then velocity measurements in pure solvents should give a constant slope for log k_0 *versus* $1/D$ plot. Such a plot is shown in Fig. 1. The values of $k_{0(\mathrm{M.F.})}$ used in Fig. 1 have been corrected[11] to mole fractions by the relation

$$k_{0(\mathrm{M.F.})} = k_0 d/W$$

where d is the density of the solvent in grams per liter, W is its molecular weight, and k_0 is the rate constant in terms of volume concentration as listed in Table I. The importance of using velocity constants based on mole fraction concentrations instead of volume concentrations, particularly when comparison is made in different solvents, has been pointed out by Scatchard[10,11] and now seems to be generally accepted. The behavior of the $k_{0(\mathrm{M.F.})}$ data in Fig. 1 indicates that salting out is not the explanation for the deviations from linearity predicted by equation (4). Apparently specific solvent influences are considerably more important than salting out effects. This explanation of specific solvent influence is also supported by the large decrease in slope with increasing non-polar solvent when log k_0 − log k_0^* is plotted[4] against $-(1/D^0 - 1/D)$ for the various solvent–water mixtures. If the rate constants in terms of volume concentrations are plotted against $1/D$, the resulting plot differs from that of the $k_{0(\mathrm{M.F.})}$ plot in so far as water, glycerol, glycol and methanol are all on a straight line. This plot is also shown on Fig. 1. Such a plot and any interpretations based upon it are open to criticism because of the concentration units used.

Values of the frequency factor B and the energy of activation E_0 for the reaction in various solvents using the k_0's corrected to mole fractions are given in Table IV. The energies of activation are relatively the same as those in Table I but the frequency factors are less than those given in Table I.

TABLE IV

CALCULATIONS BASED ON k_0'S CORRECTED TO MOLE FRACTIONS

	E_0	B
Water	23,300	13.32
Methanol	22,150	13.76
Ethanol	19,700	12.18
Isopropanol	21,000	13.04
Glycol	23,350	13.79
Glycerol	23,450	13.70

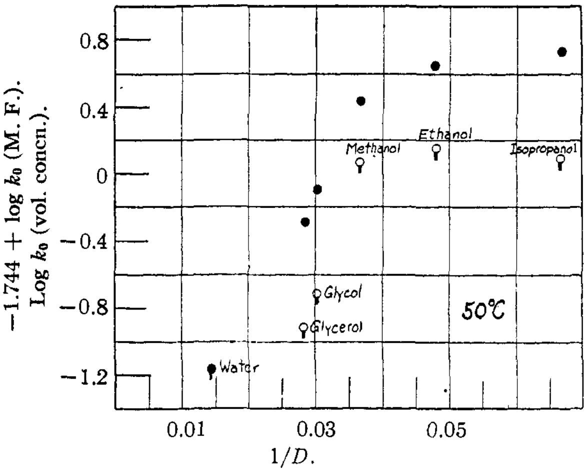

Fig. 1.—⚲, Data based on k_0 (mole fraction); ●, data based on k_0 (vol. concn.).

Using equation[4] (5), the values of E at $\sqrt{\mu}$ = 0.194

$$E = E^0 + \left(\frac{12.5 \times 10^6\, RT\, \sqrt{\mu}}{T^{3/2}D^{3/2} + 8.36 \times 10^6 \sqrt{\mu}}\right)\left(1 + \frac{d \ln D}{d \ln T}\right) \tag{5}$$

have been calculated and collected in Table II. The results are in fair agreement with the experimental E's. The theoretical prediction of a decrease in the energy of activation with increasing ionic strength when kinetic measurements are made at constant composition is upheld in all cases.

Recently Amis and Cook[12] derived an expression for the difference between the Arrhenius factor B obtained from kinetic measurements made at constant composition and from measurements made at constant dielectric constant, which when applied to the ammonium cyanate reaction predicts that $B_{\mathrm{C}} > B_{\mathrm{D}}$ at $\mu = 0$. The equation derived previously[4] for relating E_{C} to E_{D} predicts that for the ammonium cyanate reaction $E_{\mathrm{C}} > E_{\mathrm{D}}$ at $\mu = 0$. The experimental data bear out both predictions in all of the solvents considered. Calculations of $E_{\mathrm{C}} - E_{\mathrm{D}}$ from theory[4] are in better agreement with experiment when water is considered the reference solvent rather than any of the non-aqueous solvents.

Summary

1. The rate of conversion of ammonium cyanate to urea has been studied over a 30° temperature range in methanol, ethanol, isopropanol, ethylene glycol and glycerol.

2. A plot of the rate constants corrected to mole fractions against $1/D$ for the various non-

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[11] Scatchard, *Annals of the New York Academy of Sciences*, **39**, 341 (1940).

[12] Amis and Cook, THIS JOURNAL, **63**, 2621 (1941).

aqueous solvents indicates that specific solvent effects are considerably more important in accounting for the deviations from linearity predicted by Scatchard's equation than are salting out effects.

3. The Arrhenius factors B obtained from the corrected rate constants are lower than the values obtained from the rate constants based on volume concentrations, while the energies of activation are essentially the same.

4. The following predictions based on theory have been verified experimentally: (a) $E^0_C > E^0_D$; (b) $E^0_C > E_C\ (\sqrt{\mu} = 0.194)$; (c) $B^0_C > B^0_D$.

COLLEGE PARK, MD. RECEIVED SEPTEMBER 21, 1942

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 486]

The Oxidation Potential of Cerous–Ceric Perchlorates

BY MILES S. SHERRILL, CHARLES B. KING AND ROY C. SPOONER

Introduction and Plan of Investigation

The oxidation potential of an equimolal mixture of cerous and ceric salts of a given acid in the presence of that acid varies considerably with the nature of the common anion and to some extent with the concentration of the acid. Crude measurements of Bauer and Glaessner[1] showed this potential to be 1.84 volts in nitric acid solution and 1.70 volts in sulfuric acid solution. Later Kunz[2] made a thorough and accurate study of the oxidation potential of cerous–ceric sulfates in solutions of sulfuric acid. He concluded from his results that the oxidation potential, referred to the molal hydrogen electrode as zero, is 1.4435 volts in 1.0 molal, and 1.4442 volts in 0.5 molal acid solution. This seems to show that there is little change in the potential between the two concentrations of sulfuric acid.

The lack of dependence of the oxidation potential on the acid concentration over a relatively short range of acid concentration was also noted by Noyes and Garner[3] in their measurements with cerous and ceric nitrates in nitric acid solution. Thus, in solutions 2.0, 1.0 and 0.5 weight formal in nitric acid the oxidation potential was found to be 1.6104, 1.6096 and 1.6085 volts, respectively. The authors concluded from this constancy of the potential that neither complex formation nor partial hydrolysis of the cerium ions occurred over this range of acid concentration.

Smith and Getz[4] determined the oxidation potential not only with mixtures of the nitrates and sulfates, but also with those of the perchlorates, and extended the measurements to acid concentrations as high as 8 normal. With the nitrate and sulfate mixtures the potentials in the solutions of lower acid concentrations exhibited the constancy noted by the previous investigators, but at the higher concentrations decreased perceptibly. These authors attributed this decrease to the formation of complexes between the ceric ions and the acid anions. The results of their measurements with the perchlorate mixtures, however, showed a reverse effect. Thus, the potential increased steadily from 1.70 volts in 1.00 N perchloric acid solution to 1.87 volts in 8 N perchloric acid solution. Smith and Getz were of the opinion that complexes were present to a large extent even in perchloric acid solutions, although this would seem to be inconsistent with the observed increase in the oxidation potential with increasing acid concentration.

In this investigation a thorough study of the oxidation potential of mixtures of ceric and cerous perchlorates in the presence of excess perchlorate anion was made in order to ascertain what effect, if any, the acid concentration and the perchlorate ion concentration has on this potential. To this end three series of measurements consisting of several runs each were made in the following type of cell, the concentrations being expressed as weight formalities (w. f.)

$$\text{Pt} + \text{H}_2(1\ \text{atm.}),\ \text{HClO}_4(c_1\ \text{w. f.}) + \text{NaClO}_4(c_5\ \text{w. f.}),\ \text{HClO}_4(c_2\ \text{w. f.}) + \text{NaClO}_4(c_6\ \text{w. f.}) + \text{Ce(ClO}_4)_3(c_3\ \text{w. f.}) + \text{Ce(ClO}_4)_4(c_4\ \text{w. f.}),\ \text{Pt}$$

In all cases the concentration differences, $c_2 - c_1$ and $c_6 - c_5$, were kept small in order to reduce the liquid potential in the cell occasioned by these differences. It should be noted that the presence of the cerium salts in one-half the cell is partly responsible for this liquid potential. This effect

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(1) Bauer and Glaessner, *Z. Elektrochem.*, **9**, 534 (1903).

(2) Kunz, THIS JOURNAL, **53**, 98 (1931).

(3) Noyes and Garner, *ibid.*, **58**, 1265 (1936).

(4) Smith and Getz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191 (1938).