Wayne-Kerr universal bridge. Solution volumes were calculated from the solvent weights (corrected for the amount present as vapor) and the density of ammonia (0.6386 g/cm^3).[12]

Spectra.—Solutions were maintained at $-40 \pm 2°$ in quartz cells (1-, 5-, and 10-mm path length) by filling the attached cold finger with Dry Ice. Spectra were recorded on a Beckman DK-2 spectrophotometer. Solutions were prepared in Pyrex vessels attached to the cell units with Teflon valves, through which the solutions were forced into the cells with dry argon.[13]

Concentrations determined polarographically[14] after transfer to the spectral cell agreed within 3% with those calculated from the weights of sulfur and ammonia (density 0.6900 g/cm^3).[12]

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[12] C. S. Cragoe and D. R. Harper, Bureau of Standards Scientific Paper No. 430, U. S. Government Printing Office, Washington, D. C., 1921, p 313.

[13] Further details of the experimental method can be found in the Ph.D. thesis of A. P. Z.

[14] M. E. Hall, *Anal. Chem.*, **22**, 1137 (1950).

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Autocatalysis in the Copper(II) Nitrate Decomposition in Alkali Nitrate Solvents

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The autocatalytic nature of the reaction $Cu^{2+} + NO_3^- = CuO + NO_2^+$ in molten sodium nitrate–potassium nitrate equimolar solvent is confirmed. A steady-state assumption applied to the nitryl ion concentration is shown to be more applicable than the rapid equilibrium assumption used by other workers. Evidence is given to support a proposed mechanism which indicates that solid copper(II) oxide enhances the reaction between NO_2^+ and NO_3^- ions. This suggests that the catalytic nature of CuO is not specific to the Cu^{2+} ion and that CuO should catalyze any acid–base reaction in nitrate solvents for which NO_2^+ ion can be considered an intermediate species. Also other metallic oxides could possibly act as catalyst for such reactions.

Many metallic cations can generally be classed as Lux–Flood acids since they will react with basic oxyanions (oxide ion donors) to give the corresponding metal oxide and the conjugate acid of the base. Frequently the apparent acidic nature of the cation is enhanced by the relative insolubility of the metal oxide in a specific solvent.

The acid–base reaction of a divalent cation with the weak-base nitrate ion in molten alkali metal nitrate solvents can be written as $M^{2+} + NO_3^- \rightleftarrows MO + NO_2^+$. The representation of the metal ion in this equation as M^{2+} does not indicate lack of solvation of the metal ion. The manner in which various metal ions are solvated in nitrate melts has not been accurately determined, and the use of some arbitrary number of solvation anions seems unnecessarily cumbersome. Presumably the nitryl ion, a product in the above reaction, reacts further with the solvent according to the reaction $NO_2^+ + NO_3^- \rightleftarrows 2NO_2 + 0.5O_2$. There is evidence to indicate that this reaction is the rate-determining step when condensed oxyanions such as $S_2O_7^{2-}$ or $Cr_2O_7^{2-}$ are used as acids.[1] Attempts to detect the nitryl ion spectroscopically and polarographically[2] have not been successful, which suggests that the nitryl ion is not present in significant quantities in acidified alkali nitrate melts. However, recent investigations in which several organic aromatic molecules were nitrated by passing them through a $LiNO_3$–$NaNO_3$–KNO_3 ternary eutectic containing potassium pyrosulfate, a strong acid, lend support to the existence of the nitryl ion in such melts.[3]

The specific reaction between Cu(II) and NO_3^- in nitrate melts has been studied by Slama,[4] who reported that the reaction is autocatalytic in nature. The copper(II) oxide which is produced acts as a catalyst to increase the rate of disappearance of the Cu(II) ion. However, no detailed study of this catalytic process was made. It is of interest to know whether the catalytic activity of the copper oxide is specific to this reaction or whether it is a general catalyst for other acid–base reactions in molten nitrate solvents. This paper is a report of a detailed investigation of this catalytic activity in an equimolar sodium nitrate–potassium nitrate melt.

Experimental Section

Reagent grade chemicals were used unless otherwise specified. The preparation of the equimolar sodium nitrate–potassium nitrate solvent has been previously described.[5]

Anhydrous copper(II) nitrate was prepared by the reaction of nitrogen tetroxide and copper shot in anhydrous ethyl acetate according to the procedure of Addison[6] and by the reaction of nitrogen pentoxide and copper(II) nitrate trihydrate according to the procedure of Hardy and Field.[7] In this latter method the nitrogen pentoxide was prepared according to the procedure of Caesar and Goldfrank[8] since contamination with nitrogen tetroxide did not interfere with the dehydration reaction. The copper(II) nitrate–nitrogen tetroxide adducts formed were thermally decomposed under vacuum to copper(II) nitrate. The infrared spectra of the anhydrous copper(II) nitrate thus obtained agreed

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[1] (a) F. R. Duke and S. Yamamoto, *J. Am. Chem. Soc.*, **81**, 6378 (1959); (b) F. R. Duke and M. L. Iverson, *ibid.*, **80**, 5061 (1958).

[2] L. E. Topol, R. A. Osteryoung, and J. H. Christie, *J. Phys. Chem.*, **70**, 2857 (1966).

[3] R. B. Temple, C. Fay, and J. Williamson, *Chem. Commun.*, 966 (1967).

[4] I. Slama, *Collection Czech. Chem. Commun.*, **28**, 985 (1963).

[5] R. N. Kust and F. R. Duke, *J. Am. Chem. Soc.*, **85**, 3338 (1963).

[6] C. C. Addison, *J. Chem. Soc.*, 3099 (1958).

[7] C. J. Hardy and B. O. Field, *ibid.*, 3513 (1964).

[8] G. V. Caesar and M. Goldfrank, *J. Am. Chem. Soc.*, **68**, 372 (1946).

with that obtained by Ferrar and Walker[9] for anhydrous copper(II) nitrate. There was no evidence of water or N_2O_4 or N_2O_5 adduct peaks in the spectra.

The copper(II) oxide used as a catalyst was obtained both commercially and from the thermal decomposition of copper(II) nitrate. The catalytic activity of the CuO appeared to be independent of the source of the CuO but was dependent on particle size, showing greater catalytic activity as the particle size decreased. Consequently, the copper(II) oxide was screened so that the particle size ranged between 200 and 325 mesh. It was then dried at 150° for 24 hr and stored over magnesium perchlorate.

The 1-octanol used in the analysis for copper ion was reclaimed free of copper by washing first with dilute sulfuric acid, then with a sodium carbonate solution, and finally with water. It was then distilled to remove water.

The black solid product which precipitated when Cu(II) ion was added to the nitrate solvent was identified as being CuO by chemical analysis and by X-ray powder pattern comparison. The chemical analysis was done by dissolving the cooled reaction mixture in redistilled water and filtering. The black solid was washed with water and dried at 150°. It was then weighed and dissolved in dilute HCl. Aliquots of this solution were passed through a silver reductor, and the copper(I)–chloro complex was titrated with standard cerium(IV) solution. Ferroin was used as an indicator. *Anal.* Calcd for CuO: Cu, 79.9. Found: Cu, 80.3. An X-ray powder diffraction pattern was obtained from a sample which was taken directly from the melt and still contained some solvent. The resulting pattern showed only lines corresponding to CuO, $NaNO_3$, and KNO_3. The ASTM X-Ray Powder Data File was used for the comparison.

The gaseous products of the reaction of Cu(II) ion with the nitrate solvent were identified by their ir and mass spectra. The only gaseous products detected were NO_2 and O_2; other nitrogen oxides and molecular nitrogen were not detected.

The reaction vessel consisted of a 200 × 17 mm test tube into which 80–100 g of prepared solvent was added. A mechanical stirrer and a gas delivery tube extended into the solvent. The temperature of the reaction was regulated by immersing the reaction vessel in a constant-temperature bath which was controlled to within 0.5°. Varying amounts of dried copper(II) oxide catalyst, up to 10 g, were added to the solvent, after which the mixture was purged with dry purified nitrogen for several hours. A 30–60-mg sample of anhydrous copper nitrate was then added which gave an initial copper(II) ion concentration between 1.6×10^{-3} and 4.0×10^{-3} *m*. After the addition of the copper nitrate, the flow of nitrogen was stopped and the solution was stirred mechanically. The rate of mechanical stirring was sufficiently high to keep the insoluble CuO dispersed throughout the melt. It was found that the rate of reaction was independent of the stirring rate as long as the copper(II) oxide was not allowed to settle.

The rate of disappearance of Cu(II) ion was followed by withdrawing 0.3–1.5-g samples from the solution with a preheated pipet, quenching the samples in tared crucibles, and weighing accurately. The weighed samples were dissolved in redistilled water, filtered, and analyzed colorimetrically for the 1,10-phenanthroline complex of Cu(I) according to the procedure of Mellon.[10] The complex was extracted from the aqueous phase with 1-octanol. In all of the calculations, the sample weight was corrected for the copper oxide removed in the sampling process.

Results

The order of the decomposition reaction with respect to Cu(II) ion concentration, n_c, was determined for the uncatalyzed reaction by plotting the logarithm of the initial rates of disappearance of Cu(II) against the logarithm of the initial concentration for several different initial concentrations of Cu(II). The initial rates were obtained from the initial slopes of concentration *vs.* time plots for the different initial concentrations. Figure 1, line a, shows the log (initial rate) *vs.* log $[Cu(II)]_0$ plot for the uncatalyzed reaction at 328°. The slope of line a is 1.02, which indicates that n_c is 1 and that the reaction is first order in copper(II) ion concentration. Only the slope of this line is significant since the coordinates were adjusted to make the line fit on the graph with the other lines for comparison purposes. The order with respect to time, n_t, of the decomposition reaction was determined for runs made with varying initial amounts of copper(II) oxide present. This was done by graphically differentiating the plot of copper(II) ion concentration *vs.* time for each different initial amount of copper(II) oxide added. The logarithms of these slopes were then plotted against the logarithms of the copper(II) ion concentration. The slopes of the lines in these log–log plots are the order with respect to time for each different initial amount of copper(II) oxide present. Several such lines obtained at 328° are also shown in Figure 1 as lines b–d. The values of n_t were 0.48 (line d) with no initial copper oxide added, 0.75 (line c) with 5.0 g of CuO/100 g of solvent, and 0.86 (line b) with 10 g of CuO/100 g of solvent. Thus, the reaction is autocatalytic in nature ($n_t < n_c$) and CuO is the catalyst since the order with respect to time approaches in value the order with respect to copper(II) ion concentration as the initial amount of copper(II) oxide added is increased. These results are in agreement with the conclusions of Slama.[4]

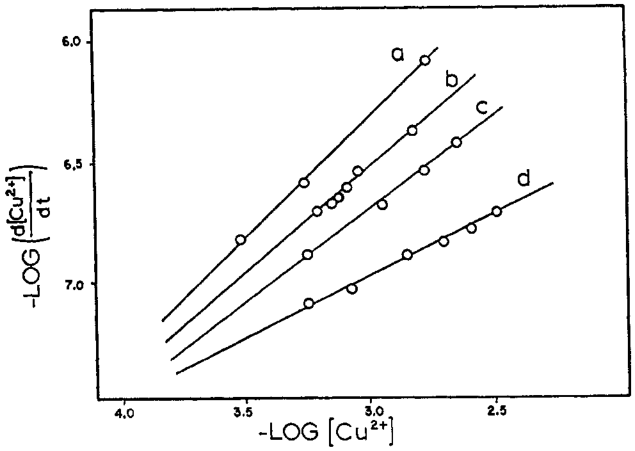

Figure 1.—Determination of order with respect to Cu^{2+} concentration, n_c, and of order with respect to time, n_t, at 328° as a function of amount of CuO present: line a, n_c = 1.02; line b, 10.0 g of CuO/100 g of solvent, n_t = 0.86; line c, 5.0 g of CuO/100 g of solvent, n_t = 0.75; line d, no CuO present, n_t = 0.48.

Discussion

In the selection of reactions which could contribute to a possible mechanism for the formation of CuO from Cu(II) in nitrate melts, the direct reaction of Cu(II) ion with O^{2-} was not considered important, since the oxide ion must be present in extremely small quantities under

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[9] J. R. Ferrar and A. Walker, *J. Chem. Phys.*, **42**, 1278 (1965).

[10] M. G. Mellon in "The Copper Reagents: Cuproine, Neocuproine, Bathocuproine," G. F. Smith, Ed., The G. F. Smith Chemical Co., Columbus, Ohio, 1958.

the acidic conditions of the solution. The reactions considered were

$$Cu^{2+} + NO_3^- \xrightarrow{k_1} CuO + NO_2^+ \quad (1)$$

$$CuO + NO_2^+ \xrightarrow{k_{-1}} Cu^{2+} + NO_3^- \quad (1a)$$

$$NO_2^+ + NO_3^- \xrightarrow{k_2} 2NO_2 + 0.5O_2 \quad (2)$$

The form of the rate law which can be developed from these reactions depends on which step is catalyzed by the presence of CuO and on the assumptions made regarding the relative magnitude of the rate constants.

If catalysis by copper(II) oxide occurs in reaction 2 and if a steady-state approximation is made regarding the nitryl ion concentration, the rate expression for the disappearance of Cu(II) can be written

$$\text{rate} = \frac{k_1k_2(1 + \alpha W)}{k_{-1} + k_2(1 + \alpha W)}[Cu^{2+}] \quad (3)$$

where α is a constant representing the catalytic activity of CuO and W is the weight of CuO added per 100 g of solvent.

If catalysis occurs in reaction 2 but $k_{-1} \gg k_2(1 + \alpha W)$, *i.e.*, if reactions 1 and 1a are in rapid equilibrium, rate expression 3 reduces to

$$\begin{aligned}\text{rate} &= \frac{k_1k_2}{k_{-1}}(1 + \alpha W)[Cu^{2+}] \\ &= K_1k_2(1 + \alpha W)[Cu^{2+}] \quad (4)\end{aligned}$$

If catalysis occurs in reaction 1 and if the steady-state assumption is made regarding the nitryl ion, the rate expression obtained would be

$$\text{rate} = \frac{k_1k_2(1 + \alpha W)}{k_{-1} + k_2}[Cu^{2+}] \quad (5)$$

The coefficients of the Cu(II) ion concentration in eq 3–5 may be considered to be pseudo-first-order rate constants which are functions of the amount of CuO catalyst present. Thus, a plot of the pseudo-first-order rate constant, k', *vs.* the amount of copper(II) oxide added would yield a curve which would asymptotically approach the value of k_1 if eq 3 were correct. If, however, eq 4 or 5 were correct, such a graph would yield straight lines with slopes of $K_1k_2\alpha$ or $k_1k_2\alpha/(k_{-1} + k_2)$, respectively.

Values of the pseudo-first-order rate constants were obtained from graphs of log [Cu^{2+}] *vs.* time, for different amounts of added CuO. The plot of these values of k' *vs.* W is shown in Figure 2 for three different temperatures. The nonlinear behavior and the leveling off at large amounts of CuO are consistent only with the pseudo-first-order rate constant indicated in eq 3, *i.e.*

$$k' = \frac{k_1k_2(1 + \alpha W)}{k_{-1} + k_2(1 + \alpha W)} \quad (6)$$

Thus it is concluded that the copper(II) oxide catalysis occurs in reaction 2 of the proposed mechanism and that the steady-state approximation made with regard to the nitryl ion concentration is more satisfactory than a rapid equilibrium assumption made with respect to reactions 1 and 1a.

The expression for the pseudo-first-order rate constant, eq 6, can be expanded into a series which takes the form

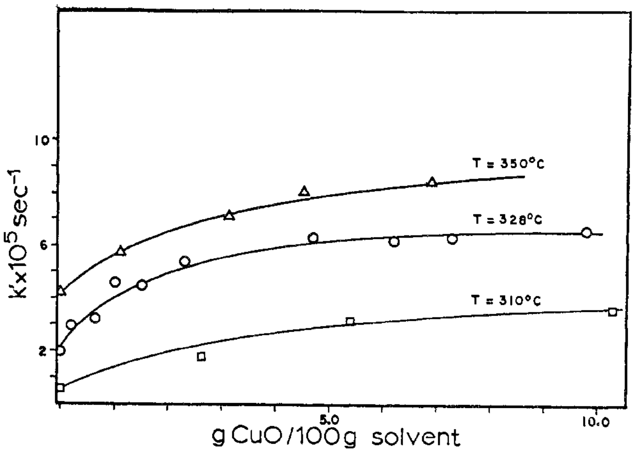

Figure 2.—Variation of pseudo-first-order rate constants with amount of copper oxide present, at several temperatures.

$$k' = k_1 + k_1k_{-1}\sum_{n=1}^{n=\infty}\frac{(-1)^n(k_{-1} + k_2)^{n-1}}{(k_2\alpha W)^n}$$

At large values of W, the second-order and higher-order terms of the series may be neglected and k' then takes the form

$$k' = k_1 - \frac{k_1k_{-1}}{k_2\alpha W} \quad (7)$$

A graph of k' *vs.* $1/W$ will then, at large W, be a straight line with an ordinate intercept of k_1 and a slope of $k_1k_{-1}/k_2\alpha$. Such a graph is shown in Figure 3 for several temperatures. Slama[4] and Duke and Yamamoto[1a] gave values of k_2 at different temperatures and Duke and Iverson[1b] gave values of k_2 for different flow rates of nitrogen. By extrapolating the nitrogen flow rate to zero and by assuming the flow rate dependency to be constant over the temperature range of this work, estimated values of k_2 may be obtained which pertain to the

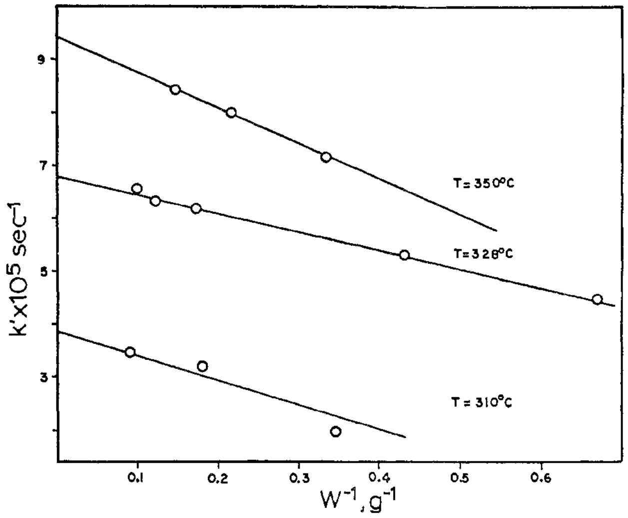

Figure 3.—Variations of pseudo-first-order rate constant, k', with $1/W$, where W is weight of CuO in grams per 100 g of solvent. The ordinate intercept is k_1.

reaction conditions of this study. Using values of k_2 obtained from Figure 3 and values of k' for the uncatalyzed reaction, the values for k_{-1} may be calculated from eq 6, since for the uncatalyzed reaction

$$k' = \frac{k_1k_2}{k_{-1} + k_2}$$

The values obtained from k_1, k_{-1}, and the ratio k_1/k_{-1} at the temperatures studied are listed in Table I. The respective activation energies and activation entropies determined from the temperature dependency of k_1 and k_{-1} for reactions 1 and 1a are 16 kcal and −46 cal deg^{-1} mol^{-1} for reaction 1 and 1.0 kcal and −57 cal deg^{-1} mol^{-1} for reaction 1a. The ratio of k_1 to k_{-1}, listed in Table I, is the equilibrium constant for the reaction $Cu^{2+} + NO_3^- \rightleftarrows CuO + NO_2^+$. $\Delta H°$ for this reaction is estimated to be 15.2 kcal. Slama,[4] who assumed a rapid equilibrium between reactions 1 and 1a, obtained a value of 39 kcal for $\Delta H°$.

TABLE I

RATE CONSTANTS FOR REACTIONS 1 AND 1a AT SEVERAL DIFFERENT TEMPERATURES

Temp, °C	10^5k_1, sec^{-1}	10^2k_{-1}, sec^{-1}	$10^3k_1/k_{-1}$
310	3.8 ± 0.4	1.3	2.9
328	6.5 ± 0.5	1.4	4.6
350	9.2 ± 0.4	1.4	6.6

The large negative entropy of activation for reaction 1 is suggestive of a coming together of like-charged species or a separation of oppositely charged species. In view of the thermal instability of the transition metal nitrates, it would seem plausible that reaction 1 is the decomposition of a dinitrate copper(II) molecule or a nitratocuprate anion to give nitryl ion and copper oxide.

That catalysis occurs in reaction 2 suggests that the catalytic activity is not specific to copper(II) oxide and that other metal oxides could possibly act as catalysts. Also copper(II) oxide could possibly act as a catalyst for other acid–base reactions in nitrate melts which involve the production of nitryl ion. Preliminary investigations have shown that Fe(III) oxide is also a catalyst for the reaction of copper(II) ion in nitrate melts. Since oxidation of Fe(III) to a higher oxidation state, such as Fe(IV) or Fe(VI), is known, it seems reasonable that such higher oxidation states could be responsible for the catalytic activity of Fe_2O_3. If this were the case, then one might consider the oxidation of Cu(II) to Cu(III) as providing a possible path for catalysis by CuO.

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Cations and Oxycations of Iodine. VI. Solutions of Some Iodine Compounds in Disulfuric Acid

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The blue solutions of iodine in oleum have been reinvestigated using both $H_2S_2O_7$ (45% oleum) and 65% oleum as a solvent by cryoscopy, conductivity, and absorption spectra measurements. It is concluded that iodine is oxidized to the I_2^+ cation although the oxidation is apparently not complete in $H_2S_2O_7$ at 25°. KI and ICl also produce the I_2^+ cation in oleum, the latter by disproportionation to I_2^+ and $I(SO_4H)_2^+$. ICl_3 ionizes to give the ICl_2^+ ion. Sulfur dioxide which is a product of the oxidation of iodine is shown to be a nonelectrolyte. There is no evidence that the +1 oxidation state of iodine is stable in oleum either as the cation I^+ or in any other form.

Introduction

The blue color of the solutions obtained by oxidizing iodine in solution in fluorosulfuric acid has been shown in part IV of this series[1] to be due to the I_2^+ cation rather than the I^+ cation. The previous evidence for the I^+ cation[2] was mainly based on the results of spectrophotometric, conductometric, and magnetic studies of solutions of iodine and iodine monochloride in 65% oleum. This paper presents the results of a new and more comprehensive study of the behavior of iodine, potassium iodide, iodine monochloride, and iodine trichloride both in 65% oleum and in 44.94% oleum which has the composition of disulfuric acid, $H_2S_2O_7$. The general properties of the disulfuric acid solvent system have recently been investigated and the results of studies of the mode of ionization of a large number of simple electrolytes have been published.[3,4] These results formed the basis of the present study of the somewhat complex ionizations of iodine compounds in this solvent. The solvent $H_2S_2O_7$ was preferred to 65% oleum which was used by Symons, *et al.*,[2] because of the complexity of this medium which has a composition between $H_2S_3O_{10}$ and $H_2S_4O_{13}$ and in fact contains

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(1) R. J. Gillespie and J. B. Milne, *Inorg. Chem.*, **5**, 1577 (1966).

(2) J. Arotsky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 12 (1961).

(3) R. J. Gillespie and K. C. Malhotra, *ibid.*, *A*, 1994 (1967).

(4) R. J. Gillespie and K. C. Malhotra, *ibid.*, *A*, 1933 (1968).