THE PHOTOLYSIS OF CRYSTALLINE NITRATES

BY PAUL DOIGAN[1] AND T. W. DAVIS

Chemistry Department, New York University, University Heights

Received October 8, 1951

The photochemical decomposition of solid nitrates under the influence of light from a high pressure mercury arc produces nitrite and oxygen. Approximate quantum yields vary from 0.002 for lithium nitrate to 0.19 for cesium nitrate in the order: $LiNO_3$, $Sr(NO_3)_2$, NH_4NO_3, $AgNO_3$, $Pb(NO_3)_2$, $La(NO_3)_3$, $Ba(NO_3)_2$, KNO_3, $La(NO_3)_3 \cdot 6H_2O$ and $CsNO_3$. The rate of photolysis is little affected by initial temperature in the range 30° to 250°. Water of hydration increases sensitivity to radiation. The rate of decomposition of the anhydrous nitrates varies in the same manner as the polarization properties of the cations.

Narayanswamy[2] observed that solid nitrates, when irradiated by light of wave length 2200 to 2500 A., decompose but the decomposition is restricted to surface layers only. He considered this localization of the reaction to be the result of back-reaction between entrapped oxygen and nitrite. Only in the surface zone could the oxygen escape and nitrite be formed. Allen and Ghormley, however, found that at low percentages of decomposition, the recombination of oxygen and nitrite within the body of the crystals is unimportant.[3] They found that barium nitrate, exposed to 1.2 mv. cathode rays, decomposed extensively. Most of the liberated oxygen remained within the crystals until the crystals were dissolved in water. Allen and Ghormley, therefore, ascribed Narayanswamy's observation to low penetration by the actinic light. We have confirmed this conclusion. We have, furthermore, determined the effect of different cations on the quantum yield and the effects of water of hydration and of temperature in the photolysis of solid nitrates.

Nitrates show two absorption bands in the range 2000–3500 Å., one starting at 3300 Å. with a peak at 3000 Å. and the other, much sharper and more intense, starting at 2630 Å. and proceeding through a maximum around 2000 Å. The processes occurring in the two regions are presumed[4] to be

$$NO_3^- \rightarrow NO_2^- + O\,(^3P_2) \qquad (1)$$

$$NO_3^- \rightarrow NO_2^- + O\,(^1D_2) \qquad (2)$$

The two bands occur in essentially the same positions for solutions, for molten potassium nitrate and for crystalline potassium nitrate.[5,6] These bands are attributable to the nitrate ion and are presumably the same for all inorganic nitrates.

Experimental

A General Electric type A-H6 high-pressure mercury arc was used as light source. The lamp operates on 840 v. and at a power level of about 1 kw. The radiation below 3000 Å. amounts to about 9% of the power input. Since the useful life of the lamps in the low wave length region was short, at most about 12 hours, it was necessary to check each lamp frequently by making standard exposures of barium nitrate. It was not enough to observe that the arc was struck, for a lamp apparently operating normally might emit no light at all effective in causing nitrate decomposition. Ellis[7] and Gillam and Morton[8] have also noted that the deterioration of mercury lamps begins in the low wave length region. Because of the short life of the arcs, individual exposure periods were kept below two hours. Longer exposures would have made it impossible to complete certain series of experiments with a single lamp.

The reaction vessel was a cylindrical fused-silica tube, 15 cm. long and 2.5 cm. in diameter. A silica-to-Pyrex graded seal was interposed between the reaction vessel and a standard-taper ground glass joint that served to attach the reaction vessel to a vacuum system. The reaction vessel was surrounded by a specially constructed furnace with two polished silica windows through which radiation was admitted. The mercury arc was permanently installed at a distance of 8 cm. from the reaction vessel. A mask made from aluminum foil with a slit 0.9 × 7.7 cm. was placed over the uppermost silica plate in order to define the incident beam.

Solutions of nitrates were used to establish the light fluxes. To keep the solutions from boiling during irradiation, it was necessary to maintain a rapid circulation of water around the reaction vessel. Warburg[9] has reported the quantum efficiency to be 0.25 at 2070 Å. and 0.17 at 2540 Å. with a sharp drop at longer wave lengths. We observed that 0.07 to 0.08 *N* solutions of KNO_3, $NaNO_3$, $Sr(NO_3)_2$ and $Ca(NO_3)_2$ undergo equal amounts of decomposition for equal irradiation. This observation lends support to the idea that light-absorption and the subsequent decomposition in solution, at least, involve principally the nitrate ion.

The salts used in this investigation were of the highest purity available. After being ground to a fine powder in a mortar, they were dried at 105° to constant weight and were stored over anhydrous calcium sulfate. Those nitrates which were obtained initially as hydrates were heated in a vacuum oven at 40° for two to four hours prior to drying at 105°. An appropriate sample was weighed into the reaction vessel and the vessel was attached to the vacuum system. The pressure was ordinarily reduced to 10^{-5} mm. and the temperature of the furnace was, if necessary, brought to the desired point before the arc was turned on.

After illumination of the salt, the gaseous product was removed by a Toepler pump and its amount was determined. The residue left in the reaction vessel was dissolved in water and the content of nitrite determined by modification of the method of Shinn.[10] Since we found the absorption curve of the coupling product formed between diazotized *p*-aminobenzene sulfonamide and N-(1-naphthyl)-ethylenediamine dihydrochloride to have a maximum at 5400 Å., we determined the extinctions at this wave length.

Barium nitrate was more extensively studied than the other salts. The amount decomposed increased linearly with time up to about 1% decomposition (the upper limit reached for this salt in our studies). Fine powder (100–200 mesh) decomposed about 30% faster than large crystals (retained by a 16 mesh screen). This difference is ascribed to more complete absorption of light by the smaller crystals.

Under similar circumstances, cesium nitrate decomposes more rapidly than barium nitrate and there is a pronounced falling off of the rate of nitrite formation after about 3% of

---

[1] General Electric Co., Pittsfield, Mass.

[2] L. K. Narayanswamy, *Trans. Faraday Soc.*, **31**, 1411 (1935).

[3] A. O. Allen and J. A. Ghormley, *J. Chem. Phys.*, **15**, 208 (1947).

[4] K. S. Krishnan and A. C. Guha, *Current Sci. (India)*, **2**, 476 (1934).

[5] I. Maslakowez, *Z. Physik*, **51**, 703 (1928); H. Ley and F. Volbert, *Z. physik. Chem.*, **130**, 308 (1927).

[6] K. Schaeffer, *Z. anorg. Chem.*, **97**, 285 (1916).

[7] C. Ellis and A. A. Wells, "The Chemical Action of Ultraviolet Rays," Reinhold Publishing Corp., New York, N. Y., 1941.

[8] A. E. Gillam and R. A. Morton, *J. Soc. Chem. Ind.*, **46**, 415 (1927).

[9] E. Warburg, *Sitz. ber. preuss. Akad. Wiss. Physik. math. Klasse*, 1228 (1918).

[10] M. B. Shinn, *Ind. Eng. Chem., Anal. Ed.*, **13**, 33 (1941).

the salt has decomposed. A rather unreliable extrapolation indicates that at about 20 to 30% decomposition the rate would become zero. Had the decomposition of the barium salt been carried as far as that of the cesium nitrate, its rate might have shown a decrease also. Such a finding would be consistent with the estimate[3] of a steady state at 40% decomposition when barium nitrate is subjected to a beam of 1.2 mv. electrons.

When the temperature of the irradiation vessel was brought initially to a value between 30° and 250°, the rate of decomposition of barium nitrate was changed less than 20%. The decomposition, therefore, is photal rather than thermal.

Narayanswamy found that different nitrates were decomposed at different rates when exposed to the same light source. We sought to confirm these effects. Our results appear in Table I. The figures represent averages of two or more determinations for each substance. The results[11] secured with different lamps were combined by comparing the decomposition of the standard substances, potassium nitrate, sodium nitrate and barium nitrate. These comparisons provide a way of correcting for the differing radiant efficiencies of the lamps. The hydrated lanthanum nitrate, it may be noted, was used as received without preliminary drying. The starting pressure of residual gas in the reaction vessel, when this salt was used, was higher than for the other substances.

TABLE I

RELATIVE RATES OF DECOMPOSITION OF SEVERAL NITRATES UNDER COMPARABLE LIGHT CONDITIONS

Salt	Relative rate of nitrite formation	Approximate quantum yield
$CsNO_3$	14.0[a]	0.19
$La(NO_3)_3 \cdot 6H_2O$	9.0	.12
KNO_3	7.5	.098
$Ba(NO_3)_2$	3.6	.048
$La(NO_3)_3$	3.1	.041
$Pb(NO_3)_2$	2.8	.037
$AgNO_3$	2.7	.036
NH_4NO_3	2.2	.030
$Sr(NO_3)_2$	1.0	.013
$NaNO_3$	0.8	.011
$LiNO_3$	0.16	.002

[a] Initial rate.

The quantum yields given in Table I are based on 0.20 as quantum yield of nitrite from nitrate solutions, and on the assumption that the absorption in the solid salts is the same as in the solution. Since no allowance has been made for scattering losses, the listed quantum yields are not of high accuracy.

It will be observed that hydrated lanthanum nitrate decomposes more rapidly than the anhydrous salt. The same effect of water of hydration in promoting photodecomposition was noted with calcium nitrate. Calcium nitrate is dispensed as the tetrahydrate. When samples of that hydrate were placed in the reaction vessel and pumped for varying lengths of time before illumination, the following amounts of nitrite were obtained: with no pumping, 5.0 mg.; after 12 hours, 1.7 mg.; after 17 to 71 hours, 1.3 mg.

Narayanswamy listed the nitrates in order of increasing sensitivity to light as follows: NH_4NO_3, $Pb(NO_3)_2$, $Al(NO_3)_3$, $Cd(NO_3)_2$, $Ba(NO_3)_2$, $Sr(NO_3)_2$, $NaNO_3$, KNO_3.

We found the order: $LiNO_3$, $NaNO_3$, $Sr(NO_3)_2$, NH_4NO_3, $AgNO_3$, $Pb(NO_3)_2$, $La(NO_3)_3$, $Ba(NO_3)_2$, KNO_3, $La(NO_3)\cdot 6H_2O$, $CsNO_3$.

It is possible that some of the disagreement between the two lists arises from differences in degree of desiccation of the salts. Narayanswamy does not report whether or how he dried his materials, and even if they were initially dry he presumably exposed them in open vessels with an accompanying possibility that some absorbed moisture from the air before and during illumination. Our procedure avoided such uncertainty.

Discussion

The rates of decomposition of the alkali nitrates as given in Table I increase from lithium to cesium, that is, they increase with increasing size or with decreasing field strengths of the cations. Ammonium nitrate is observed to be more stable than potassium nitrate, although these two salts have nearly equal molar volumes. However, as other properties show[12] the polynuclear ammonium ion does not exhibit the same field strength as an alkali ion of comparable size. Also of interest is the result that silver nitrate decomposes faster than sodium nitrate, although their molar volumes do not differ much. The polarization properties of silver ion, however, which has an 18-electron outer shell, are very different from those of sodium ion, which is of the noble gas type.[13]

Similar interrelations can be found for the nitrates of doubly charged cations. Strontium nitrate decomposes more slowly than barium nitrate because the field of barium ion is weaker than that of strontium ion. On the other hand, although strontium and lead nitrates have nearly equal molar volumes, their decomposition rates are different because lead does not have a noble gas type structure.

The positions in Table I of the nitrates of strontium and barium as compared with those of sodium and potassium are in accord with the relative tightening, derived from refractivity data on silicates,[14] exerted on anions by the doubly and singly charged cations.

While the above facts clearly indicate that the decomposition of the nitrate ion is dependent on the field strength of the cation, to which it is bound in the anhydrous crystal, it would be premature to draw further conclusions concerning the nature of the interionic interaction involved. It suffices to add that the greater decomposition rate of the nitrate ion in aqueous solution as well as in hydrated nitrates, as compared to the anhydrous nitrates, might be related to the fact that the field of the water dipoles, separating the nitrate ions from the cations, is weaker than that of the latter.

Narayanswamy has suggested that the effect of the absorbed light is to detach oxygen atoms from nitrate ions.[2] Once released the oxygen atoms seem to have two principal courses open to them. They can either combine with each other or they can react with other nitrate ions,

$$NO_3^- + O \rightarrow NO_2^- + O_2 \qquad (3)$$

A possible reversal of the initial dissociation would be

$$NO_2^- + O \rightarrow NO_3^- \qquad (4)$$

The absence of any considerable temperature effect in the photolysis suggests that reactions (3) and (4) either do not occur or occur with equal energies of activation.

The oxygen atoms, in any event, seem to end up as oxygen gas. Only part of the gas appears during illumination; the rest can be pumped off in the course of two hours following the cessation of illumination provided the salt is kept at 100°. At the

---

[11] More complete tables are listed in the Ph.D. thesis of P. Doigan, New York University, 1950.

[12] K. Fajans and O. Johnson, *J. Am. Chem. Soc.*, **64**, 668 (1942).

[13] K. Fajans, *Ceram. Age*, **54**, 288 (1949).

[14] K. Fajans and N. J. Kreidel, *J. Am. Ceram. Soc.*, **31**, 105 (1948)

end of two hours of pumping, the recovered gas closely matches the amount of oxygen expected on the basis of the nitrite analysis. Villars found only oxygen in the gases from photolyzed nitrate solutions.[15] We were unable to identify any other component in the gas coming from the crystals. Essentially all the gas recovered was soluble in alkaline pyrogallol and essentially all of it was absorbed by hot copper.

Acknowledgment.—The authors gratefully acknowledge the assistance of Dr. Seymour Lewin and of Dr. Kasimir Fajans in the preparation of this report.

[15] D. S. Villars, *J. Am. Chem. Soc.*, **49**, 328 (1927).

AN EXPLANATION OF "TACKYPYKNOSIS"

BY R. N. THOMPSON

Calgon, Inc., Pittsburgh, Pennsylvania

Received October 15, 1951

It has been shown that the equilibrium torque measured by a rotational type viscometer on a thixotropic system is a function of the rate of shear and the amount of thixotropy in the system at that rate of shear. There will be a definite equilibrium torque for each shearing rate and these torques will only approach one another as the difference between the rates of shear approaches zero. The phenomenon which Van Wazer chose to call "tackypyknosis" is really not a distinct phenomenon. It is thixotropy and should be recognized as such.

Van Wazer and Besmertnuk[1] in their paper on the "Action of Phosphates on Kaolin Suspensions" reported an anomalous flow phenomenon of deflocculated kaolin suspensions which they chose to call "tackypyknosis." They observed that when a deflocculated kaolin suspension "is contained in a viscosimeter in which the shearing rate is adjustable and the resulting shearing force is measured, it is found that upon the application of a fast rate of shear to the material, the resulting torque rises sharply and then slowly decreases from a high value to a constant value. If the shearing rate is suddenly lowered, the shearing force quickly falls away and then slowly increases again to practically the same constant value. When the speed remains constant, the shearing forces reach a given value which appears to be practically independent of shearing rate."

This phenomenon has been investigated by means of both a MacMicheal viscometer and a Hagan viscometer which is capable of producing much higher rates of shear than the MacMicheal instrument. In this investigation the Green[2] system of rheological analysis was used. The MacMicheal viscometer had instrumental constants $S = 0.011$ and $C = 0.027$ and could produce a maximum rate of shear of about 10 reciprocal seconds. The Hagan viscometer is a rotation type of viscometer wherein the bob is driven and the shearing force is measured on the cup. The instrumental constants for the cup and bob used were $S = 0.0036$ and $C = 0.0180$ and under these conditions produced a maximum shearing rate of about 533 reciprocal seconds.

Procedure

Paper coating grade kaolins were used in this investigation. They were deflocculated with sufficient glassy sodium metaphosphate so that the resulting suspensions were very fluid at 68% total solids. Rheograms were obtained for the suspensions on both the MacMicheal and Hagan viscometers, thus obtaining the flow characteristics at both low and high rates of shear.

Three rheograms were obtained by first running the up curve to some predetermined rate of shear, allowing the shearing force to reach equilibrium at that rate of shear, and then running the down curve. Secondly, after allowing the kaolin suspension to return to its original condition, the above procedure was repeated only running the up curve to a higher predetermined rate of shear. Thirdly, after allowing the kaolin suspension to return again to its original condition, an up curve was run to the second or higher rate of shear; the rate of shear was held constant until the shearing force had reached equilibrium and then the rate of shear was decreased to the first or lower shearing rate which was again held constant until the shearing force had reached an equilibrium value.

Results

Figure 1 shows the rheograms obtained on the MacMicheal viscometer with a 68% total solids kaolin suspension. The angular velocity in radians per second may be converted into rate of shear in reciprocal seconds by multiplying by the constant 2.3. By plotting the time to go from T' to T_E' and the time to go from T_x to T_E, Fig. 2 is obtained which corresponds to Van Wazer's example of "tackypyknosis." Figure 3 shows the rheograms obtained on the Hagan viscometer for the same kaolin suspension as reported in Fig. 1. The angular velocity in radians per second may be converted into rate of shear in reciprocal seconds by multiplying by the constant 4.8. It will be noted that T_E and T_E' no longer approach one another in value as they did at low rates of shear. The point T_E in Figs. 1 and 3 can be reached by several paths.

Discussion of Results

Green[2] has derived the equation for the equilibrium torque at a given rate of shear to be

$$T_E = T - \frac{B}{S}\,\omega \ln\left(\frac{t_E}{t}\right) \qquad (1)$$

where T_E = equilibrium torque, T = maximum torque on up curve, B = coefficient of thixotropic breakdown with time, ω = angular velocity of cup or bob, t = time required to produce up curve, t_E = time required to reach equilibrium torque at a

---

[1] J. R. Van Wazer and E. Besmertnuk, THIS JOURNAL, **54**, 89 (1950).

[2] Henry Green, "Industrial Rheology and Rheological Structure," New York, N. Y., 1949.