CONTRIBUTION OF THE BASIC RESEARCH LABORATORY,
USAERDL, FORT BELVOIR, VIRGINIA

The Role of Impurities in the Decomposition of Molten Potassium Azide

BY HEINRICH EGGHART

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The thermal decompositions of undoped and doped potassium azide melts were studied. The decomposition rates were increased orders of magnitudes by doping with certain transition metal salts. First rapid initial reactions occurred which can be represented by the equation $M^{2+}_{impurity} + 2N_3^- \rightarrow M^0 + 3N_2$. Some metals precipitated immediately after their formation. Others remained dissolved for certain periods, the lengths of which were temperature dependent. Dissolved metals were without influence while precipitated metals catalyzed the decomposition. With group VIII metals the same activation energy was observed with precipitated as well as massive metals. Group I-B metals showed a lower activation energy when precipitated which was attributed to a decrease in the temperature at which vacancies can be formed in the d band by thermal activation.

Introduction

The decomposition of inorganic azides has been studied extensively by Garner and co-workers, Tompkins and co-workers, and others. This field has been reviewed also by Evans, Yoffe, and Gray where the references of most papers which appeared before 1959 can be found.[1] Most widely investigated were decompositions of the type $MN_3(s) \rightarrow M(s) + {}^3/_2N_2$. The metals (M) formed were found to autocatalyze the decomposition since less energy is required to excite an electron first from an azide ion into the metal and subsequently to the cation.[2] The decomposition of alkali azides is a special case since the metals which are formed are liquid at the temperatures of decomposition and evaporate if the experiments are conducted under vacuum. Accordingly, higher activation energies were found when potassium azide was decomposed under a hard vacuum as compared to decomposition in an atmosphere of 16 mm. potassium metal vapor pressure, namely 49 *vs.* 41 kcal./mole, respectively.[3]

Alkali azides are relatively stable in comparison to other azides. Little or no energy is evolved when they decompose to metal and nitrogen. Potassium, rubidium, and cesium azides melt before decomposition becomes appreciable. The autocatalytic effect also occurred in molten potassium azide, which was indicated by experiments to be described in this paper. Nevertheless, the decomposition rates of potassium azide melts were very small near the melting point of 345° and comparatively small even at temperatures above 400°. Activation energies of approximately 50 kcal./mole have been found. The autocatalytic effect of potassium was by far surpassed by the catalytic influences of other metals which had been added to potassium azide.[4] Metals having vacancies in the d-band were especially active catalytically and lowered the activation energy for the potassium azide melt decomposition to about 32 kcal./mole.

This paper deals mainly with the mechanism by which ionic impurities effect the decomposition of potassium azide melts. Two different reaction phases were observed. First the impurity cations were reduced to the respective metals and a stoichiometric amount of azide ions decomposed. Then the impurity metals catalyzed the decomposition of the molten azide according to the normal decomposition reaction: $2KN_3(l) \rightarrow 2K(l) + 3N_2(g)$. Group I-B metals when formed in the potassium azide melt facilitated the decomposition with a lower activation energy than massive group I-B metals. An explanation for this is proposed. Some metals remained dissolved in the potassium azide melt for certain periods and did not show any catalytic influence in this state, which will be discussed also.

Experimental

The experiments were conducted in a high vacuum decomposition apparatus which was described in more detail previously.[4] It included two liquid nitrogen cold traps. One was part of the system in which the nitrogen accumulated; the other was between this system and the pumps. Samples usually weighing less than 1 mg. were placed on the rotatable glass spoon of the apparatus. After outgassing, the samples were dropped into the reaction vessel (Pyrex or quartz tubes in a vertical position) which was surrounded by a brass block, the temperature of which was held constant electronically. The decomposition was followed by automatically recording the increase in nitrogen pressure measured by an Alphatron gauge. The experiments were conducted in the range from 0.1 to 100 μ. The time it took between dropping the sample into the reaction tube until melting occurred was less than 1 sec. The activation energies were determined by decomposing a number of samples at different temperatures as well as with the split-run technique. With this method the decomposition rates at different temperatures could be obtained with one and the same sample. After the rate was measured at a certain temperature the sample was quickly brought to room temperature by removing the heated brass block from the sample tube. When the brass block attained the next higher or lower temperature it was put again into the position in which it surrounded the reaction vessel. After the time needed for temperature equalization the rate was measured again. The experiments were considered satisfactory only when the same activation energy was obtained in a series with rising and falling temperatures. Doped samples were prepared by mixing potassium azide and metal salts in a little agate vial with a Spex mixer mill. The three-dimensional action of this mixer mill ensured a perfectly homogeneous mixture within a few

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(1) B. L. Evans, A. D. Yoffe, and P. Gray, *Chem. Rev.*, **59**, 515 (1959).

(2) N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," Clarendon Press, Oxford, 1948, p. 264.

(3) P. W. M. Jacobs and F. C. Tompkins, *Proc. Roy. Soc.* (London), **A215**, 265 (1952).

(4) H. Egghart, *Inorg. Chem.*, **2**, 364 (1963).

minutes of mixing time. Potassium azide samples were prepared which contained metal salts in concentrations from 0.1 to 5.6 mole %.

Results and Discussion

Experiments with Undoped Potassium Azide.—Long induction periods have been observed in the decomposition of solid potassium azide.[5] Now similar decomposition curves with induction periods, accelerating stages, and constant rates during the main part of decomposition were found in experiments with molten potassium azide at temperatures between 380 and 450°. This may be seen in curve A of Figure 1, where nitrogen evolution curves expressed in fractional decomposition are drawn. It was also observed that the lengths of the induction periods were dependent on the outgassing times to which the samples had been subjected. For instance, in experiments at 404° the induction periods were shortened from about 85 to 35 min. if the samples were outgassed 24 hr. instead of only 1 hr. (at 10^{-6} mm. pressure and room temperature). The decomposition apparatus included a liquid nitrogen cold trap. Nevertheless, the induction periods seemed to be caused by residual water traces. This was indicated by mass spectrometric studies which showed that the gas formed during the induction periods contained considerably more hydrogen than the gas evolved during the main decomposition where nitrogen almost exclusively was formed. These experiments probably indicate that the autocatalytic process is suppressed during the induction period due to consumption of newly formed potassium metal by reaction with water traces. During the accelerating stage the amount of potassium metal increases. Finally the decomposition rate becomes constant, probably due to an equilibrium between potassium metal formation and evaporation.

Experiments with Doped Potassium Azide.—When melts of potassium azide containing ionic impurities were decomposed the rates were increased by several orders of magnitude. The decomposition process was dominated by the impurities and no effects due to water were observed. The impurities participated in the decomposition in two different steps. First in a rapid reaction which lasted no longer than a few seconds a volume of nitrogen was evolved which was proportional to the amount of metal salt added and to the valency of its cation. No potassium metal was formed, which was also indicated by mass spectrometric analysis of the gas evolved from samples containing salts with water of crystallization. The peak in the mass spectrum, indicating traces of hydrogen, was not larger than that observed with pure potassium azide. Much of the water of crystallization possibly escaped before reaction occurred. However, more time seemed necessary to expel all the water from the melt. Neither in the initial reaction nor in the following catalytic decomposition was it important whether metal halides or metal sulfates (water-free or containing water of crystallization) were used as additives. All these observations indicated that the over-all chemical change in the initial reactions consisted of an electron transfer from the azide ions to the impurity cations and can be described by the equation: $M^{2+}{}_{\text{impurity}} + 2N_3^- \rightarrow M^0 + 3N_2$. These reactions were very fast in molten potassium azide but could be studied at lower temperatures where potassium azide is solid or in low melting fused salts. Some metals precipitated rapidly after their formation and the catalytic decomposition began at the same time. Other metals remained dissolved in the potassium azide melt for certain lengths of time and very little nitrogen was evolved during these intervals. The catalytically accelerated decomposition process $2KN_3(l) \rightarrow 2K(l) + 3N_2(g)$ was observed only after nucleation occurred and the metal particles appeared. The formation of metal from the impurity ions was confirmed by X-ray analysis. Also the gas evolved during the catalytic decomposition consisted almost exclusively of nitrogen as shown by mass spectrometry.

Group VIII Impurities.—In decomposition of samples doped with nickel, cobalt, palladium, rhodium, or platinum the precipitation of the metal particles could be seen to follow the discharge of the respective ions immediately. At the same time the catalytic decomposition of the potassium azide began. Therefore, the phase of electron transfer to the impurity ions and the catalytic decomposition phase could not be distinguished in many of these cases, as for instance in curve C of Figure 1, which represents a cobalt salt doped sample. However, the complete stoichiometric proportionality between metal ion added and nitrogen evolved during the initial reaction could always be established by performing the experiments at temperatures too low for the catalytic decomposition to occur. At these temperatures the samples were in the solid state. Between 110 and 120°, samples containing 2.2 mole % of cobalt salt needed a few minutes for the cobalt metal and nitrogen forming reaction, and then the nitrogen evolution ceased entirely. Under a hot-stage microscope these reactions could be followed by observing the metal formation. The pellets turned gray on sporadic spots which then became the centers of enhanced reaction. Thereafter, the samples began to show dark gray, pale gray, and almost white areas before the whole pellet became entirely dark gray. The nitrogen evolution curves of these solid-state reactions of potassium azide with metal salts had the sigmoid shape typical for interface reactions. From the temperature coefficient of these curves an activation energy of 45 kcal./mole was obtained for cobalt as well as nickel salt doped samples. This activation energy is associated with the reaction in the solid state only, as was found in experiments carried out in low melting fused salts as media.

The activation energy for decomposition of potassium azide melts which had been doped with cobalt or nickel salts was found to be in the range of 30.5 ± 1 kcal./mole. Practically the same value was obtained when

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[5] W. E. Garner and D. J. B. Marke, *J. Chem. Soc.*, 657 (1936).

potassium azide melts were decomposed on surfaces of massive cobalt and nickel metals which were added as powders. The experiments with doped samples as well as with samples containing massive metals were performed with the individual-run and split-run technique in the temperature range from 348 to 380°. The results with both methods were the same within the limits of experimental accuracy.

The catalytic decomposition rates increased proportionally when the concentrations of impurity salt were increased. This shows that the size of the cobalt and nickel particles formed was independent of the metal ion concentration in the potassium azide.

When iron salts were added to potassium azide the phase of electron transfer to the impurity ions and the phase of catalytic decomposition were separated by intervals during which no appreciable nitrogen evolution occurred. This can be seen in curve B of Figure 1. The amount of nitrogen evolved during the initial reaction indicated that the iron ions were discharged. However, the melt did not turn black rapidly due to metal formation, but became brownish and remained clear. At temperatures not too much above the melting point of potassium azide these induction periods lasted several minutes for samples which contained 1 mole % of ferrous salts and became shorter as the ferrous salt concentration was increased. With 5 mole % samples the induction periods were only seconds long. This dependence of the length of the induction periods on the original metal salt concentrations indicated that the induction period was the time required for nucleation and precipitation of the iron metal formed in the initial reaction. When samples containing ferric salts were studied in the usual temperature range of 348 to 380° no precipitation of iron metal and no termination of the induction periods was observed. To achieve the precipitation of the iron in a reasonable length of time the experiments had to be carried out at temperatures above 400°. The length of the induction periods was not only dependent on the initial metal salt concentrations but also on the temperature. However, in the case of samples doped with iron salts the reproducibility of this temperature dependency was not good enough to obtain reliable activation energy data for the processes leading to nucleation. When the iron metal finally precipitated this occurred within a relatively short interval and the catalytic decomposition of the potassium azide began at the same time.

It was observed that doubling the concentration of iron salt did not double the rate of the catalytic decomposition. This can be seen in Table I, where each k value, taken from Arrhenius plots, represents an average of approximately 20 experiments. The accuracy of these rates was better than ±4% even if the reduction of error by averaging over 20 experiments was not taken into account. The results shown in Table I indicate a dependence of the size of the iron particles formed on the initial ferrous ion concentration.

TABLE I

DEPENDENCE OF THE CATALYTIC DECOMPOSITION RATE ON THE INITIAL ADDITIVE CONCENTRATION

Moles of $FeSO_4$/100 mole of KN_3	k^a
1.4	5.8×10^{-3}
2.8	8.3×10^{-3}
5.6	11.2×10^{-3}

[a] Decomposition rate in change of fractional decomposition per second at 372°.

An activation energy of 30.5 ± 1 kcal./mole was found in decomposition of iron salt doped samples when the split-run technique was used. With the individual-run technique a 10 kcal./mole higher activation energy was obtained. The result with the split-run technique must be considered to be the correct one, since the activation energy found in decomposition on massive iron metal was 31 ± 1 kcal./mole regardless of which technique was used. All these experiments were conducted in the same temperature range of 348–380°. Different results with the split-run technique and the individual-run technique were only observed with doped samples which showed delayed nucleation of the metal. In these samples the decomposition velocities at different temperatures were apparently influenced by an additional factor which was eliminated by the use of the split-run technique. The divergent results obtained with the individual-run and split-run technique in samples doped with iron salts may be understood with the following considerations. The length of the induction periods was found to be dependent on the concentration of the metal salt added and on the temperature. It appears reasonable to assume that the size of the iron particles formed, and thereby the specific surface of the iron present, was temperature-dependent also. With the individual-run method the metal particles were formed at different temperatures. Therefore, different samples probably had different surface areas of catalyst available. For this reason, only the split-run technique could be expected to give correct results in the samples where delayed nucleation occurred. It was not possible to prove this conclusion by direct observation since a relatively small difference in particle size is sufficient to cause the described effect. In addition, electron microscopic observations showed that the particles were rather conglomerated.

The parts of the curves which belong to the catalytic decomposition phase had a similar shape for all of the group VIII metals which were studied. There was a fast rate at the beginning which decreased until a constant rate was reached (Figure 1, curves B and C). The same decomposition characteristic was found previously in decompositions of potassium azide melts on surfaces of massive rather than reaction-formed group VIII metals. It was shown that this shape of the decomposition curves was determined by changes in the frequency factors only and the activation energies were the same on all parts of the curves.[4] When additional potassium azide was dropped on residues of previously decomposed doped samples (performed by using three rotatable glass spoons provided in the apparatus) the decomposition curves were linear from the origin, thereby indicating zero-order kinetics. In the decomposition of potassium azide on metal powders of known specific surface it was found that the frequency factors increase in the sequence Ni < Co < Fe.[4] With potassium azide samples containing nickel, cobalt, or iron salts in equal molar ratios a similar trend of the specific activities was found. This probably indicates that the particle sizes of these metals, when formed within the potassium azide melts, did not differ very much from each other.

Chromium Ions as Impurity.—Doping of potassium azide with chromous salts resulted in curves similar to those found with ferrous salt doped samples but there was relatively more decomposition during the induction periods. With chromic salts the induction periods were extremely long, as has been observed also with ferric salts. The activation energy for potassium azide decomposition of chromous salt doped samples was 35 kcal./mole as determined with the split-run technique. The melts remained greenish and clear during the induction periods. The solid which finally precipitated was not black or dark gray as in the doped samples described before, but brown. X-Ray patterns of the decomposition residues showed the major lines of chromium nitride (β-Cr_2N). From the viewpoint of thermodynamics, nitride formation can also be expected when ions of the transition elements to the left of chromium in the periodic table are present in potassium azide melts. Chromium metal powder has not been found to catalyze the decomposition of potassium azide melts, a fact which was attributed to the oxide layers shielding this metal and which cannot be reduced by decomposing potassium azide.[4] With chromium salts the chemical potential is sufficient for reduction to the metal by potassium azide but more energy is gained by the nitride formation.

Group I-B Impurities.—With potassium azide samples containing cuprous or cupric salts, with or without water of crystallization, the initial reaction and the catalytic decomposition were separated by long intervals. Curve D of Figure 1 represents the experiments with copper salt doped samples. The part of the curve which belongs to the initial reaction was not drawn because it falls on the ordinate. The ratio of nitrogen evolved during the initial reaction to the total nitrogen formed showed, with good accuracy, that all copper ions were discharged. For samples with 5.4 mole % $CuSO_4$ the induction period before the start of the catalytic decomposition was 125 min. at 402° compared to 15 min. at 450°. From the temperature dependence of the length of these induction periods an activation energy of 41 ± 2 kcal./mole could be obtained. This may be considered the activation energy required by the processes leading to nucleation and subsequent precipitation of copper metal in the melt. The high value is not surprising in view of the high interaction energies calculated for metal–molten salt systems.[6] It appears unlikely that the copper is in any kind of aggregated state during the induction periods, since metal particles of 10–20 Å. diameter are known to behave as normal metals insofar as chemisorption and catalysis are concerned.[7] In addition, particles of this size probably would be large enough to act an nuclei for precipitation. Also, stable colloid suspensions of metals in molten salts are not known.[8] The existence of induction periods showed that no homogeneous catalysis took place and that the catalytic decomposition of molten potassium azide occurred on surfaces of solid metals only. The high interaction energies between metals and molten salts indicate electronic changes.[6] Therefore, metal atoms dissolved in molten salts may be quite different from normal metal atoms and their inability to catalyze the decomposition of the potassium azide melts is understandable. Probably, metal atoms which interact very little with the melt would be poor catalysts also, since adsorption of more than one azide ion seems likely to be important for decomposition to occur easily.

The transition time from the induction period to the catalytic decomposition phase (acceleration period) lasted a number of seconds with potassium azide containing iron salts and a number of minutes with samples containing copper salts. A relationship seems indicated between the catalytic properties of the formed metals and the decomposition velocity and the rate of precipitation, respectively. However, the activation energy obtained from the temperature dependence of this transition time was the same as the one obtained from the temperature dependence of the lengths of the induction periods and different from the activation energy for catalytic decomposition.

When potassium azide was doped with gold chloride ($HAuCl_4 \cdot H_2O$) no induction periods occurred. Nevertheless, the end of the initial reaction was clearly indicated by a sharp change in the slope of the nitrogen evolution curves. The reason was the comparatively small rate of catalytic decomposition even at temperatures between 400 and 450°. Curve E of Figure 1 is for potassium azide doped with 2.7 mole % gold chloride. Like curve D, curve E also appears not to begin in the origin because the initial reaction is too fast to be drawn separately from the ordinate.

The catalytic decomposition of potassium azide melts on reaction-formed copper, as well as gold, took place with a constant rate up to about a fractional decomposition of $\alpha = 0.6$, which can be seen in Figure 1. The same decomposition characteristic has been observed also in the presence of massive copper.[4] The activation energy for decomposition of potassium azide on surfaces of reaction-formed copper or gold was found to be 34 ± 2 kcal./mole using the split-run technique at temperatures between 348 and 380°.

In Figure 2 the Arrhenius plots are shown which

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(6) L. E. Topol, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963.

(7) P. W. Selwood, "Adsorption and Collective Paramagnetism," Academic Press, New York, N. Y., 1962.

(8) IU. K. Delimarskii and B. F. Markov, "Electrochemistry of Fused Salts," The Sigma Press, Washington, D. C.

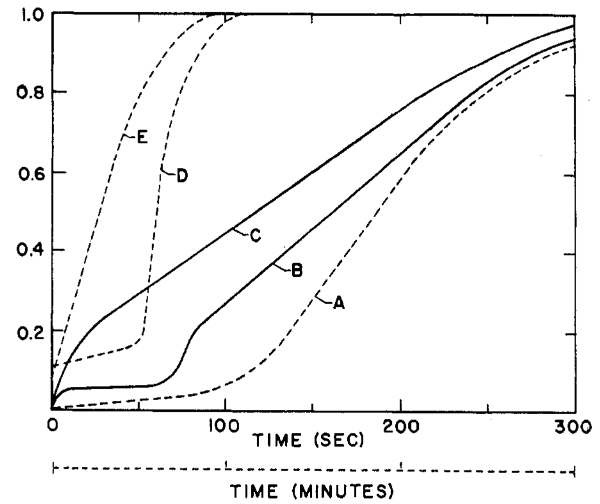

Figure 1.—Decomposition curves of undoped and doped potassium azide samples: curve A, fractional decomposition, α, *vs.* time (min.), undoped KN_3, 404°; curve B, fractional decomposition, α, *vs.* time (sec.), KN_3 doped with 2.8 mole% $FeSO_4$, 354°; curve C, fractional decomposition, α, *vs.* time (sec.), KN_3 doped with 2.2 mole % $CoCl_2$, 370°; curve D, fractional decomposition, α, *vs.* time (min.), KN_3 doped with 5.4 mole % $CuSO_4$, 428°; curve E, fractional decomposition, α, *vs.* time (min.), KN_3 doped with 2.7 mole % $HAuCl_4 \cdot H_2O$, 428°.

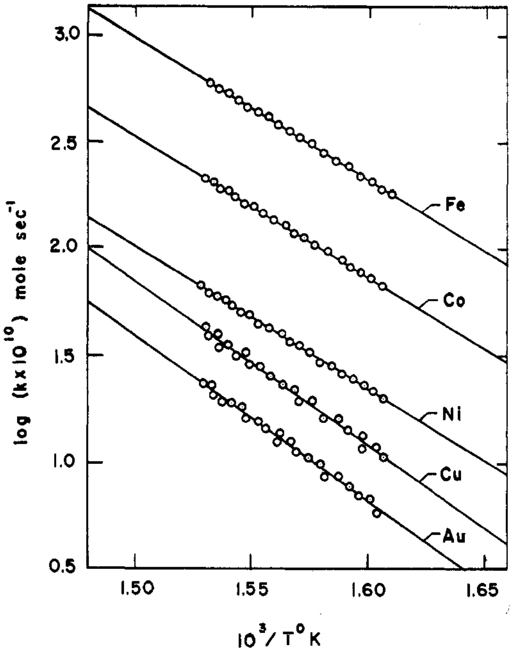

Figure 2.—Arrhenius plots. Logarithms of the decomposition rate (mole sec.$^{-1}$) of doped potassium azide samples *vs.* $1/T$(°K.). Plot Fe—KN_3 doped with 0.1 mole % iron salts. Plot Co—KN_3 doped with 0.1 mole % cobalt salts. Plot Ni—KN_3 doped with 0.2 mole % nickel salts. Plot Cu—KN_3 doped with 1.0 mole % copper salts. Plot Au—KN_3 doped with 2.0 mole % gold salts.

belong to the catalytic decomposition phase of the metal salt doped potassium azide samples discussed in this paper. The rates were measured in split-run experiments conducted in the linear main region of the catalytic decomposition and at temperatures between 348 and 380°. They were obtained with samples containing 0.1 mole % iron and cobalt salts, 0.2 mole % nickel salts, 1 mole % copper salts, and 2 mole % gold salts. The use of these various impurity concentrations was necessary because of the large differences in the catalytic activities. It would have been impossible to observe the catalytic effect in samples doped with gold salts in the low concentrations used, for instance, in iron salt doped samples. The rates were expressed in moles of potassium azide decomposed per second, as calculated from the rate of nitrogen pressure increase in the apparatus. The specific surfaces of the metals formed in the potassium azide melts were not known.

Comparison of the Activation Energies for Potassium Azide Melt Decomposition on Surfaces of Massive and Reaction-Formed Metals.—The activation energies for potassium azide melt decomposition on iron, cobalt, nickel, and copper metal powders (massive metals) have been determined previously with the individual-run method.[4] In order to provide a good basis for comparison, the activation energies with these massive metals, as well as with massive gold, were now determined with the split-run technique. An activation energy of 31 ± 1 kcal./mole was found with the massive metals belonging to group VIII, 41 ± 2 kcal./mole with massive copper, and 40 ± 2 kcal./mole with massive gold. These data are shown in Table II together with the results obtained with the metal salt doped samples. All values of Table II were obtained with the split-run technique at temperatures between 348 and 380°. The results in this table clearly show that the activation energies were in the same range with massive as well as with reaction-formed group VIII metals. Such was not the case with copper and gold although these metals had the same decomposition characteristics in either form. The over-all catalytic activity was comparatively small in any case. However, the activation energies with the reaction-formed group I-B metals were considerably lower than with these metals in massive form.

TABLE II

ACTIVATION ENERGIES FOR CATALYTIC DECOMPOSITION OF MOLTEN POTASSIUM AZIDE ON SURFACES OF MASSIVE METALS AND OF METALS FORMED WITHIN POTASSIUM AZIDE MELTS

	Massive metal	Metal formed within the KN_3 melt
Fe	31 kcal./mole	30.5 kcal./mole
Co	31 kcal./mole	30.5 kcal./mole
Ni	31 kcal./mole	30.5 kcal./mole
Cu	41 kcal./mole	34 kcal./mole
Au	40 kcal./mole	34 kcal./mole

Higher catalytic activities with chemically-produced group I-B metals as compared to the respective massive metals have been found in other systems also.[9-14]

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(9) K. F. Bonhoeffer, A. Farcas, and K. W. Rummel, *Z. physik. Chem.*, **B21**, 225 (1933).

(10) H. S. Taylor and H. Diamond, *J. Am. Chem. Soc.*, **57**, 1251 (1935).

(11) A. Couper, D. D. Eley, M. J. Hulatt, and D. R. Rossington, *Bull. Soc. Chem. Belges*, **67**, 343 (1958).

(12) D. A. Dowden, *ibid.*, **67**, 439 (1958).

(13) I. Uhara, S. Yanagimoto, K. Tani, and G. Adachi, *Nature*, **192**, 867 (1961).

(14) I. Uhara, S. Yanagimoto, K. Tani, G. Adachi, and S. Teratani, *J. Phys. Chem.*, **66**, 2991 (1962).

To account for the results it was necessary to assume that the surfaces of group I-B metals which were chemically prepared have paramagnetic properties not possessed by the usual bulk metal.[10] Potassium azide melts were found to decompose with a considerably lower activation energy on surfaces of iron, cobalt, or nickel than on surfaces of copper or gold. This was attributed to the vacancies in the d-band which are not present in group I-B metals.[4] However, according to Dowden[12] the lattice defects present in chemically-formed group I-B metals can reduce the gap between the top of the d-band and the Fermi level. In massive group I-B metals the defects anneal out to a very low concentration, but when chemically formed they can be maintained by impurities and occlusions. Later, experimental evidence for these theories was given by Uhara and co-workers,[13–15] who studied the decomposition of diazonium chloride and other reactions on copper as catalyst. The catalytic activity was increased when copper was cold worked and returned during annealing to the original activity at about the same temperature where the strain energy was released. This happened with 99.96% pure copper at temperatures around 350°, but at 430° with copper containing a few tenths of a per cent of impurities. Chemically-produced copper showed even higher catalytic activity than cold worked copper. This was attributed to an enhanced defect structure which is also thermally more stable. Copper prepared by low current density electrolysis of copper sulfate solutions was catalytically like massive copper. When prepared at high current densities catalytically active copper was obtained. This was probably due to the occlusions and lattice distortions which are usually found in metals obtained by high current density electrolysis.[16,17]

The metals formed within the potassium azide melts can be expected to possess distorted structures. This was indicated by the diffuseness of their X-ray patterns, which may be due to both small grain size and lattice distortions. With group I-B metals this may lead to decreased energetic requirements for the formation of holes in the d-band by thermal activation which may explain the lower activation energies for potassium azide melt decomposition on surfaces of reaction-formed copper and gold.

Acknowledgment.—The author wishes to thank Dr. S. B. Newman, National Bureau of Standards, for the electron microscopic pictures and Mr. A. J. Coleman, Basic Research Laboratory, for mass spectrometric analysis of gas samples.

[15] I. Uhara, S. Kishimoto, T. Hikino, Y. Kageyama, H. Hamada, and Y. Numata, *J. Phys. Chem.*, **67**, 996 (1963).

[16] M. Schlötter, *Discussions Faraday Soc.*, **31**, 1177 (1935).

[17] L. Wright, H. Hirst, and J. Riley, *ibid.*, **31**, 1253 (1935).

Contribution from the Department of Chemistry,
The University of Texas, Austin, Texas 78712

The Iodides of Phosphorus. I. Lewis Basicity and Structure[1]

By A. H. Cowley and S. T. Cohen

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The Lewis base behavior of PI_3 and P_2I_4 has been investigated by testing their reactivity toward the boron halides. Consistent with the order of Lewis acidity $BF_3 < BCl_3 < BBr_3 < BI_3$ it was found that neither of the phosphorus iodides reacted with BF_3 or BCl_3, but that both reacted with BBr_3 and BI_3. No reaction was observed with SO_2. The complexes isolated were $PI_3 \cdot BBr_3$, $P_2I_4 \cdot 2BBr_3$, and $PI_3 \cdot BI_3$. The isolation of $P_2I_4 \cdot 2BBr_3$ confirms the earlier work of Tarible. The structures of the complexes were investigated by infrared spectral measurements. The infrared spectra of PI_3 and P_2I_4 were also determined. The conformation of P_2I_4 in solution is probably *gauche.*

Introduction

There is comparatively little information in the literature concerning the simple chemistry of the phosphorus iodides, PI_3 and P_2I_4. This is remarkable when it is realized that these compounds have been known since the middle of the nineteenth century.[2] We have examined various aspects of the chemistry of these halides, such as their Lewis basicity, structures in solution, and some metathetical reactions. In this paper we discuss their reactivity toward the boron halides and sulfur dioxide and also their structures in carbon disulfide solution. Previous work[3,4] has shown that the donor behavior of a phosphorus trihalide depends on the electronegativity of the halogen substituents. Thus, PCl_3[5] and PBr_3[5] form 1:1 adducts with the Lewis acid BBr_3, while PF_3 appears to have no donor properties if only σ bonding is considered.[6] It was therefore of interest to test the basicity of PI_3

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[1] Presented in part at the 20th Southwest Regional American Chemical Society Meeting, Shreveport, La., Dec. 1964.

[2] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1928, Vol. 8, pp. 1038–1041.

[3] D. S. Payne, *Quart. Rev.* (London), **15**, 173 (1961).

[4] R. R. Holmes, *J. Chem. Educ.*, **40**, 125 (1963).

[5] R. R. Holmes, *J. Inorg. Nucl. Chem.*, **12**, 266 (1960).

[6] Various complexes are known which presumably involve π bonding, such as $Ni(PF_3)_4$, $PF_3 \cdot BH_3$, and $(PF_3)_2PtCl_2$. See ref. 3 and also R. W. Parry and T. C. Bissot, *J. Am. Chem. Soc.*, **78**, 1524 (1956).